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### ON THE APPLICATION OF INTEGRAL EQUATION TO THE EXPANSION OF AN ARBITRARY FUNCTION IN A SERIES OF SPECIAL FUNCTIONS

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#### SUMMARY

In this paper I have selected two special functions  $J_n^2(x)$  and  $J_0^2(2nt)$  which may be expressed as integral equations  $J_n^2(x) = \frac{2}{\pi} \int_0^{\pi/2} J_{2n}(2x \sin \theta) d\theta$  and  $J_0^2(2nt) = \frac{2}{\pi} \int_0^{\pi/2} J_0(2nt \sin \theta) d\theta$ .

Expressing  $F(x)$  as the integral equation  $F(x) = \frac{2}{\pi} \int_0^{\pi/2} \varphi(x \sin \theta) d\theta$  and expanding  $\varphi(x \sin \theta)$  in a series of  $J_{2n}(2x \sin \theta)$  or  $J_0(2x \sin \theta)$  we get the expansion of  $F(x)$  in a series of  $J_n^2(x)$  or  $J_0^2(nx)$ .

It is easier to expand a function in a series of orthogonal special functions. Here I shall show how the method of integral equation may be used to expand a function in a series of some special functions.

1. We know\*  $J_n^2(x) = \frac{2}{\pi} \int_0^{\pi/2} J_{2n}(2x \sin \theta) d\theta$ . Let  $F(2x) = \sum_0^\infty A_{2n} J_n^2(x) = \frac{2}{\pi} \int_0^{\pi/2}$

$\varphi(2x \sin \theta) d\theta$  where  $\varphi(2x \sin \theta) = \sum_0^\infty A_m J_m(2x \sin \theta)$

\* Watson, Bessel functions, p. 32

$$\begin{aligned} J_n^2(x) &= \frac{2}{\pi} \int_0^{\pi/2} J_{2n}(2x \sin \theta) d\theta \\ &= \frac{1}{\pi} \int_0^\pi J_0(2x \sin \psi) \cos 2 \sin \psi d\psi \end{aligned}$$

By Schlömilch's integral equation we have  $\varphi(2x) = F(0) + 2x \int_0^{\pi/2} F'(2x \sin \psi) d\psi$

By Maclaurin's method we see that

$$A_{2n} = 2n \sum_{m=0}^{<n} \frac{\varphi^{2n-2m}(0)}{[2n \cdot 2m]} 2^{2n-2m} \frac{(2n-m-1)!}{m!} \quad (n \leq 1)$$

Example. Let  $F(2x) = J_0(2x)$ .

$$\text{Then } \varphi(2x) = J_0(0) + 2x \int_0^{\pi/2} J_0'(2x \sin \psi) d\psi$$

$$= 1 - 2x \int_0^{\pi/2} J_1(2x \sin \psi) d\psi$$

$$= \cos(2x).$$

$$A_{2n} = 2(-1)^n; a_0 = 1^*$$

Hence

$$J_0(2x) = J_0^2(x) - 2J_2^2(x) + 2J_4^2(x)$$

Test of Convergence:—

$$\text{Let } F(2x) = \sum_{n=0}^{\infty} \frac{F^{2n}(0)}{[2n]} 2^{2n} x^{2n} \text{ be convergent.}$$

$$\text{Then } \varphi(2n) = F(0) + \sum_{n=0}^{\infty} \frac{F^{2n}(0)}{[2n-1]} (2x)^{2n} \frac{[1/2][n]}{2[n+\frac{1}{2}]}$$

will be convergent if

$$\text{Lt}_{n \rightarrow \infty} \frac{F^{2n+2}(0)}{2F^{2n}(0)} \frac{(2x)^2}{(2n+1)(n+\frac{1}{2})} \rightarrow 0 \text{ i.e. if the Maclaurin's series for } F(x)$$

be convergent. Then the series  $\sum_0^{\infty} A_{2n} J_n^2(x)$  will be uniformly convergent for  $(x) \leq R$  where  $R$  is less than the radius of convergence of the series for  $\varphi(2x)$  if  $0 \leq x \leq \pi/2$  and  $F(x)$  be even function of  $x$  which can be expanded into convergent Maclaurin's series.

$$2 \text{ We know }^* J_0^2(2nt) = \frac{2}{\pi} \int_0^{\pi/2} J_0(2nt \sin \theta) d\theta$$

\* Neumann has obtained in a different way in which the co-efficients are difficult to obtain.

\* Watson. l. c., p. 525.

$$\begin{aligned}\text{Let } F(2t) &= \sum_0^\infty A_{2n} J_0^2(2nt) = \frac{2}{\pi} \int_0^{\pi/2} d\theta \sum_0^\infty A_{2n} J_0(2nt \sin \theta) \\ &= \frac{2}{\pi} \int_0^{\pi/2} \varphi(2t \sin \theta) d\theta.\end{aligned}$$

$$\text{where } \varphi(2t \sin \theta) = \sum_0^\infty A_{2n} J_0(2nt \sin \theta)$$

$$\text{Then as before in 1, } \varphi(x) = F(0) + x \int_0^{\pi/2} F'(x \sin \psi) d\psi \text{ and } a_{2n}$$

$$= \frac{2}{\pi} \int_0^\pi u \cos 2nu \left\{ \int_0^1 \frac{\varphi'(u\xi) d\xi}{\sqrt{1-\xi^2}} \right\} du$$

$$n=1, 2, \dots$$

$$a_0 = \frac{2}{\pi} \int_0^\pi \left\{ \varphi(0) + v \int_0^1 \frac{\varphi'(v\xi) d\xi}{\sqrt{1-\xi^2}} \right\} du$$

Example.

$$\text{Let } F(2t) = \frac{8t^2}{\pi}.$$

$$\varphi(x) = x \int_0^{\pi/2} \frac{4}{\pi} \cdot x \sin \psi d\psi = \frac{4}{\pi} x^2.$$

$$a_0 = \frac{2}{\pi} \int_0^\pi u \left\{ \int_0^1 \frac{8}{\pi} \cdot \frac{u\xi}{\sqrt{1-\xi^2}} d\xi \right\} du = \frac{16}{\pi^2} \cdot \frac{\pi^3}{3} = \frac{16\pi}{3}.$$

$$a_{2n} = \frac{2}{\pi} \int_0^\pi u^2 \cos 2nu \cdot \frac{8}{\pi} du = \frac{16}{\pi^2} \int_0^\pi u^2 \cos 2nu du = \frac{8}{\pi n^2}$$

Hence

$$\frac{8t^2}{\pi} = \frac{16\pi}{3} J_0^2(2t) - \frac{8}{\pi} \sum_{n=1}^\infty \frac{J_0^2(2nt)}{n^2}$$

The Test of Convergency:—

The series for  $\varphi(x)$  will be convergent as before.

$F(x)$  should be even function of  $x$  which can be expanded in convergent Maclaurin's series.

$F(0) + x \int_0^{\pi/2} F'(n \sin \psi) d\psi$  must be continuous Homo to  $n$ .

And  $\int_0^{\pi/2} F'(x \sin \psi) d\psi + x \int_0^{\pi/2} F''(x \sin \psi) \sin \psi d\psi$  exists and is continuous for  $0 \leq x \leq \pi$ .

### *References*

1. Watson, "Bessel functions," p. 32.
2. Watson, l. c., p. 525

# ON CERTAIN INTEGRALS AND EXPANSIONS CONTAINING BESSEL AND LEGENDRE'S ASSOCIATED FUNCTIONS

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## SUMMARY

Applying operational calculus to certain series I have found some new definite integrals and expansions containing Legendre's Associated functions and Bessel functions.

Dr. S. Mitra\* has considered certain definite integrals containing Legendre's functions and Bessel functions. Here I shall consider certain definite integrals and expansions containing Legendre's Associated functions and Bessel functions. The results, which are new, have been starred. The following results are necessary :—

$$(1) \quad \dagger \sqrt{\frac{2}{\pi}} Q_m(t) = \int_0^\infty e^{-tp} e I_{m+\frac{1}{2}}(p) \frac{dp}{\sqrt{p}}.$$

$$(2) \quad \ddagger \frac{\sin 2 \sqrt{\alpha(1-Z)}}{\sqrt{1-Z}} = \frac{1}{2\pi i} \int_{c-ia}^{c+ia} \frac{e^{-1/p(1-Z)+p\alpha} dp}{p^{\frac{1}{2}}}$$

$$(3) \quad \S x J_0(\sqrt{u}x) = \sum_{n=0}^{\infty} (4n+2) P_n(1-2u) J_{2n+1}(x) - 1 \leq u \leq 1. \text{ i.e., } 0 \leq u \leq 1$$

$$(4) \quad \parallel \frac{J_{m+\frac{1}{2}}(u)}{u^{m+\frac{1}{2}}} = (-1)^m \sqrt{\frac{2}{\pi}} \left( \frac{d}{u du} \right)^m \frac{\sin u}{u}.$$

We know that 
$$\frac{1}{t-Z} = \sum_{n=0}^{\infty} (2n+1) P_n(Z) Q_n(t)$$

Hence 
$$\frac{(1-Z^2)^{m/2}}{(t-Z)^{m+1}} = \sum_{n=0}^{\infty} \frac{2n+1}{m} P_n^m(Z) Q_n(t)$$

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\* Dr. S. Mitra, "On certain integrals and expansions involving Bessel functions",  
Bulletin Calcutta Math. Soc. Vol. XXV, No 2, p. 81.

† Watson's "Theory of Bessel functions," p. 387.

‡ Dr. S. Mitra, l. c., p. 92.

§ Bateman, "On expansion of an arbitrary function in a series of Bessel functions."  
Mess. Math. 36 (1907) pp. 31—37.

|| Watson, Theory of Bessel functions, p. 54.

Or,

$$\int_{-1}^1 \frac{t (1-Z^2)^{m/2} P_n^m(Z) dz}{(t-Z)^{m+1}} = \frac{2}{m} \frac{n+m}{n-m} t Q_n(t) \quad (5)$$

From (1) we have after interpretation

$$\sqrt{\pi/2} \frac{I_{m+\frac{1}{2}}(p)}{\sqrt{p}} = \frac{1}{2\pi i} \int_{c-ia}^{c+ia} t e^{pt} Q_m(t) dt \quad (6)$$

Again 
$$e^{pz} = \frac{1}{2\pi i} \int_{c-ia}^{c+ia} \frac{t e^{pt} dt}{t-Z}$$

Therefore 
$$\frac{e^{pz} p^m}{m} = \frac{1}{2\pi i} \int_{c-ia}^{c+ia} \frac{t e^{pt} dt}{(t-z)^{m+1}} \quad (7)$$

Hence, interpreting (5) and using (6), (7) we have

$$* \int_{-1}^1 e^{pz} P_n^m (1-Z^2)^{m/2} P_n^m(Z) d_z = \sqrt{\frac{2\pi}{p}} \frac{n+m}{n-m} I_{n+\frac{1}{2}}^{(p)}$$

Or, 
$$\int_{-1}^1 p^{-(n+\frac{1}{2})} e^{-1/p} (1-Z) (1-Z^2)^{m/2} P_n^m(Z) d_z$$
  

$$= \sqrt{2\pi} \frac{n+m}{n-m} e^{-1/p} I_{n+\frac{1}{2}}(p) \quad (8)$$

From (2) we have

$$(-1)^m \frac{d^m}{d(1-Z)^m} \frac{\sin 2\sqrt{\alpha(1-Z)}}{\sqrt{1-Z}}$$

$$= \frac{1}{2\pi i} \int_{c-ia}^{c+ia} e^{-1/p(1-Z)+pa} \frac{dp}{p^{m+\frac{1}{2}}} \quad (9)$$

After interpreting (8) and using (9) we have

$$\int_{-1}^1 \frac{(-1)^m d^m}{d(1-Z)^m} \frac{\sin 2\sqrt{\alpha(1-Z)}}{\sqrt{1-Z}} (1-Z^2)^{m/2} P_n^m(Z) dZ$$

$$= \sqrt{2} \pi J_{n+\frac{1}{2}}^2(\sqrt{2\alpha}) \quad (10)$$

Let  $Z=1-2y^2, x=\sqrt{2\alpha}$

Using (4) in (10) we have

$$* \int_0^1 (1-y^2)^{m/2} y^{\frac{1}{2}} J_{m+\frac{1}{2}}(2xy) P_n^m(1-2y^2) dy$$

$$= \frac{\sqrt{\pi}}{2} \frac{J_{n+\frac{1}{2}}^2(x)}{x^{m+\frac{1}{2}}} \quad (11)$$

Again 
$$\frac{(-1)^m (1-Z^2)^{m/2} (t^2-1)^{m/2}}{(t-Z)^{2m+1}}$$

$$= \sum_{0}^{\infty} \frac{2n+1}{2m} P_n^m(Z) Q_n^m(t)$$

Hence\* 
$$\int_{-1}^1 \frac{(-1)^m (1-Z^2)^{m/2} (t^2-1)^{m/2}}{(t-Z)^{2m+1}} P_n^m(Z) dz$$

$$= \frac{2}{2m} \frac{n+m}{n-m} Q_n^m(t)$$

Let  $t = 1+2a^2$ ,  $Z = 1-2y^2$ ,  $a > 0$

$$\frac{(-1)^m y^m (1-y^2)^{m/2} (1+a^2)^{m/2} a^m}{2(a^2+y^2)^{2m+1}}$$

$$= \sum_{0}^{\infty} \frac{(2n+1)}{2m} P_n^m(1-2y^2) Q_n^m(1+2a^2)$$

Then\* 
$$\int_0^1 \frac{(-1)^m y^{m+\frac{1}{2}} (1-y^2)^m a^m (1+a^2)^{m/2}}{(a^2+y^2)^{2m+1}} J_{m+\frac{1}{2}}(xy) dy$$

$$= \frac{\sqrt{\pi}}{2m} \sum_{0}^{\infty} \frac{2n+1}{x^{m+\frac{1}{2}}} J_{n+\frac{1}{2}}(x) Q_n^m(1+2a^2)$$

by using . (11)

From (3)

$$2^m u^m x (1-u^2)^{m/2} \left( -\frac{d}{4u du} \right)^m J_0(ux)$$

$$= \sum_{0}^{\infty} (4n+2) P_n^m(1-2u^2) J_{2n+1}(x)$$

\*  $r(1-u^2)^{m/2} J_m(ux)$

$$= 2^m \sum_{0}^{\infty} (4n+2) P_n^m(1-2u^2) J_{2n+1}(x)$$

\*  $x \int_0^1 (1-u^2)^{m/2} u J_m(ux) P_n^m(1-2u^2) du$

$$= \frac{2^m}{n-m} J_{2n+1}(x) \quad \dots \quad (12)$$

$$\begin{aligned}
 & *(-1)^m a^m (1+a^2)^{m/2} \int_0^1 u^{m+1} (1-u^2)^m x J_m(ux) du \\
 & = \frac{2^{m+1}}{(2m)!} \sum_{n=0}^{\infty} \frac{(n+m)!}{(n-m)!} J_{2n+1}(x) Q_n^m (1+2a^2) \times (2n+1)
 \end{aligned}$$

by using (12)

$$\begin{aligned}
 & * \int_0^1 x (1-u^2)^m u^{\frac{1}{2}} J_m(ux) J_{m+\frac{1}{2}}(2ux) du \\
 & = \sqrt{\pi} 2^{m-1} \sum_{n=0}^{\infty} \frac{(4n+2) J_{2n+1}(x) J_{n+\frac{1}{2}}^2(x)}{x^{m+\frac{1}{2}}}
 \end{aligned}$$

using (11)

### References

1. Bateman, "On expansion of an arbitrary functions in a series of Bessel functions." *Mess. Math.* 36 (1907), pp. 31-37.
2. Mitra, S., "On certain integrals and expansions involving Bessel functions" *Bulletin Calcutta Math. Soc.*, Vol. XXV, No. 2, p. 81.
3. Mitra, S., l. c., p. 92.
4. Watson, "Theory of Bessel functions," p. 387.
5. Watson, "Theory of Bessel functions," p. 54.



# ON THE SUMMABILITY OF THE CONJUGATE SERIES OF THE DERIVED FOURIER SERIES

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## SUMMARY

The object of the present note is to establish a theorem for  $(C, K)$  summability of  $\sum_{n=1}^{\infty} n (an \cos nt + bn \sin nt)$  the conjugate series of the differentiated Fourier series, analogous to the theorems of Verblunsky and Takahashi for the Fourier series, allied series of the Fourier series, and derived Fourier series.

Before coming to the main theorem I have first defined certain notations and proved certain results, which have been used later in the articles 1.2 and 1.3. In the article 2.1 the main theorem has been enunciated which is proved in four parts, first for  $p=0$ , secondly for  $p=n$ , where  $n$  is a positive integer, then for  $p=a$ , where  $a$  is a positive proper fraction and lastly for  $p=n+a$ .

In the end of the article 2.5, another theorem, which is an immediate corollary to the above theorem, is given. In the next article the same theorem has been put in a different form. Lastly in theorem IV I have tried to find out the necessary and sufficient condition for  $(C, K)$  summability of the series under discussion, when certain condition is satisfied at a particular point.

**1.1** Let  $f(t)$  be absolutely integrable (L) and periodic (with period  $2\pi$ ) and let its Fourier series be

$$(1.1) \quad \frac{1}{2} a_0 + \sum_{n=1}^{\infty} (an \cos nt + bn \sin nt)$$

Then the series

$$(1.2) \quad \sum_{n=1}^{\infty} n (an \cos nt + bn \sin nt)$$

is called the conjugate series of the differentiated Fourier series.

The summability  $(C, K)$  for  $K>1$  and  $K>0$  of the series (1.2) has been discussed by Miss Sayers (5), Takahashi (4) and K. L. Gupta (6). The object of the present note is to establish a theorem for  $(C, K)$  summability of (1.2), analogous to the theorems of Verblunsky (1) and Takahashi (3) for Fourier series, allied series of the Fourier series and derived Fourier series.

I take this opportunity of expressing my best thanks to Prof. S. Charan, Head of Mathematics Department, for his kindness in giving me all possible

facilities for carrying on my studies and to Mr. M. L. Misra, for his kind interest and advice in the preparation of this paper.

1.2. We use the following notations.

$$(1.3) \quad \phi(t) = f(x+t) + f(x-t)$$

$$(1.4) \quad \theta(t) = \frac{1}{\pi} \int_t^{\infty} \frac{\phi(u)}{u^2} du$$

$$(1.5) \quad \psi_0(t) = \psi(t) = \theta(t) - S$$

$$(1.6) \quad \psi_1(t) = \frac{1}{t} \int_0^t \psi_0(u) du$$

$$(1.7) \quad \psi_r(t) = \frac{1}{t} \int_0^t \psi_{r-1}(u) du. \quad \text{Where } r \text{ is an integer.}$$

If  $r = n + \alpha$ , where  $n$  is zero or a positive integer and  $0 < \alpha < 1$  we write

$$(1.8) \quad \psi_r(t) = \frac{1}{t^\alpha} \int_0^t \psi_n(u) (t-u)^{\alpha-1} du$$

$$(1.9) \quad \psi_1^*(t) = \frac{1}{t} \int_0^t |\psi(u)| du.$$

and

$$(1.10) \quad \gamma_{1+k}(t) = \int_0^t (1-u)^k \cos tu du.$$

In this discussion we take the  $k^{\text{th}}$  Rieszian mean instead of taking  $k^{\text{th}}$  Cesaro mean, since both are equivalent (7).

The  $k^{\text{th}}$  Rieszian mean of (1.2) is

$$(1.11) \quad \lim_{w \rightarrow \infty} \frac{w}{(k+1)} \cdot \frac{1}{\pi} \int_0^{\infty} [f(x+t) + f(x-t)] \frac{d}{dt} \left[ w t \gamma_{k+2}(wt) \right] dt.$$

1.3 First we consider the integral (1.11). In virtue of (1.3) it is equal to

$$\lim_{w \rightarrow \infty} \frac{w}{(k+1)} \cdot \frac{1}{\pi} \int_0^{\infty} \phi(t) \frac{d}{dt} \left[ w t \gamma_{k+2}(wt) \right] dt.$$

$$(1.12) = \lim_{w \rightarrow \infty} \frac{w}{(k+1)} \frac{1}{\pi} \int_0^{\infty} \frac{d}{dt} [\theta(t)] t^2 \frac{d}{dt} \left[ w t \gamma_{k+2}(wt) \right] dt.$$

Since  $\frac{d}{du} [w \gamma_{k+2}(u)] = (k+1) [\gamma_{k+1}(u) - \gamma_{k+2}(u)]$

$\therefore$  (1.12) is equal to

$$\begin{aligned} & \lim_{w \rightarrow \infty} \int_0^{\infty} \frac{d\theta(t)}{dt} (wt)^2 [\gamma_{k+1}(wt) - \gamma_{k+2}(wt)] dt. \\ &= \lim_{w \rightarrow \infty} \int_0^{\infty} \frac{d}{dt} \theta(t) (wt)^2 \gamma_{k+1}(wt) dt - \lim_{w \rightarrow \infty} \int_0^{\infty} \frac{d}{dt} \theta(t) (wt)^2 \gamma_{k+2}(wt) dt. \\ &= \lim_{w \rightarrow \infty} [I_1 - I_2] \end{aligned}$$

Again since  $\frac{d}{du} [u^2 \gamma_{k+2}(u)] = -k(k+1) \gamma'_k(u)$

On integrating by parts, we have

$$(1.13) \quad I_1 = \left[ \theta(t) (wt)^2 \gamma_{k+1}(wt) \right]_0^{\infty} + k(k-1) w \int_0^{\infty} \theta(t) \gamma'_{k-1}(wt) dt.$$

And because  $\gamma_{k+1}^{(8)}(t)$  and all its derivatives are uniformly bounded for all  $t$  and as  $t \rightarrow \infty$

$$\gamma_{k+1}(t) = O\left(\frac{1}{t^2}\right) \quad (k \geq 1)$$

and  $\theta(t) = 0(1)$  when  $t = \infty$  and for small

$$t > 0 \quad \theta(t) = O\left(\frac{1}{t}\right)$$

the expression under the square brackets on the right hand of (1.13) vanishes

$$\therefore I_1 = k(k-1) w \int_0^{\infty} \theta(t) \gamma'_{k-1}(wt) dt.$$

Now it is evident that for  $\eta > 0$  where  $\eta$  is an arbitrary number

$$\lim_{w \rightarrow \infty} w \int_{\eta}^{\infty} \theta(t) \gamma_{k+1}^1(wt) dt = 0 \text{ for } K > 2.$$

$$\therefore \lim_{w \rightarrow \infty} I_1 = \lim_{w \rightarrow \infty} k(k-1) w \int_0^{\eta} \theta(t) \gamma'_{k-1}(wt) dt.$$

similarly, putting  $(k+1)$  for  $k$ .

$$\lim_{w \rightarrow \infty} I_2 = \lim_{w \rightarrow \infty} k(k+1) w \int_0^{\eta} \theta(t) \gamma'_k(wt) dt.$$

$$\therefore \lim_{w \rightarrow \infty} (I_1 - I_2) = \lim_{w \rightarrow \infty} kw \int_0^{\eta} \left[ (k-1) \gamma'_{k-1}(wt) - (k+1) \gamma'_k(wt) \right] \theta(t) dt.$$

Therefore in order to prove that the series (1.2) is summable (C, K) to S at a point  $t=x$ , we have to prove that

$$\lim_{w \rightarrow \infty} kw \int_0^{\eta} \left[ (k-1) \gamma_{k-1}(wt) - (k+1) \gamma_k(wt) \right] \theta(t) dt = S$$

But we know that

$$\lim_{w \rightarrow \infty} kw \int_0^{\eta} \left[ (k-1) \gamma_{k-1}(wt) - (k+1) \gamma_k(wt) \right] dt = 1.$$

$\therefore$  The above equation reduces, in virtue of (1.5), to

$$\lim_{w \rightarrow \infty} kw \int_0^{\eta} \left[ (k-1) \gamma_{k-1}(wt) - (k+1) \gamma_k(wt) \right] \psi(t) dt = 0$$

$$\text{or (1.14) } \lim_{w \rightarrow \infty} \int_0^{\eta} \left[ \chi_{k-1}(wt) - \chi_k(wt) \right] dt = 0$$

Where  $\chi_k(wt) = k(k+1) w \gamma'_k(wt) \psi(t)$ .

**2.1. Theorem 1.** The series allied with the derived Fourier series of an absolutely integrable and periodic function  $f(t)$ , with period  $2\pi$ , is summable  $(C, p+2+\delta)$  to  $S$  at  $t=x$  for all positive  $p$  and  $\delta > 0$ , if

$$\frac{1}{t} \int_0^t \psi_p(u) du = O(1)$$

$$\text{and } \frac{1}{t} \int_0^t |\psi_p(u)| du = O(1)$$

**2.2.** We shall prove this theorem in 4 parts, first for  $p=0$ , secondly for  $p=n$ , where  $n$  is a positive integer, thirdly for  $p=\alpha$ , where  $\alpha$  is a positive proper fraction and lastly for  $p=n+\alpha$ .

For  $p=0$  the theorem I can be enunciated as,

**Theorem I (a).** If

$$(2.1) \quad \psi_1(t) = \frac{1}{t} \int_0^t \psi(u) du = O(1)$$

$$\text{and } (2.2) \quad \psi_1^*(t) = \frac{1}{t} \int_0^t |\psi(u)| du = O(1)$$

$$\text{then, } (2.3) \quad \lim_{\omega \rightarrow \infty} \int_0^\eta [\chi_{1+\delta}(\omega t) - \chi_{2+\delta}(\omega t)] dt = 0$$

By (1.14)

$$\text{or} \quad \lim_{\omega \rightarrow \infty} [I_1 - I_2] = 0.$$

$$\begin{aligned} \text{Now } I_1 &= (2+\delta)(1+\delta)\omega \int_0^\eta \psi(t) \gamma'_{1+\delta}(\omega t) dt \\ &= (2+\delta)(1+\delta)\omega \left[ \int_0^{\lambda/\omega} + \int_{\lambda/\omega}^\eta \right] \psi(t) \gamma'_{1+\delta}(\omega t) dt \\ &= (2+\delta)(1+\delta) [I_1' + I_1'']. \end{aligned}$$

First we consider

$$I_1' = \omega \int_0^{\lambda/\omega} \psi(t) \gamma'_{1+\delta}(\omega t) dt.$$

On integrating by parts

$$\begin{aligned} I_1' &= \lambda \psi_1(\lambda/\omega) \gamma'_{1+\delta}(\lambda) - \omega^2 \int_0^{\lambda/\omega} t \psi_1(t) \gamma''_{1+\delta}(\omega t) dt \\ &= O(1) - O[\omega^2 \int_0^{\lambda/\omega} t dt] \quad \text{By (2.1)} \\ &= O(1) \end{aligned}$$

$$\begin{aligned}
\text{and } |I_1'| &\leq c\omega \int_{\lambda/\omega}^{\eta} |\psi(t)| \frac{dt}{(\omega t)^{1+m}} \quad \text{where } m = \min [2, \delta] \\
&\leq \frac{c}{\omega^m} \int_{\lambda/\omega}^{\eta} |\psi(t)| \frac{dt}{t^{1+m}} \\
&\leq \frac{c}{\omega^m} \left[ \frac{\psi_1^*(t)}{t^m} \right]_{\lambda/\omega}^{\eta} + \frac{c}{\omega^m} \int_{\lambda/\omega}^{\eta} \frac{\psi_1^*(t)}{t^{1+m}} dt. \\
&\leq \frac{c}{\omega^m} \frac{\psi_1^*(\eta)}{\eta^m} + \frac{c\psi_1^*(\lambda/\omega)}{\lambda^m} + \frac{c}{\omega^m} O \left[ \left( \frac{1}{t^m} \right)^{\eta}_{\lambda/\omega} \right] \\
&\leq O \left( \frac{1}{\omega^m} \right) + O \left( \frac{1}{\lambda^m} \right) + O \left( \frac{1}{\lambda^m} \right) + O \left( \frac{1}{\omega^m} \right) \text{ By (2.2).}
\end{aligned}$$

This tends to zero if  $\lambda \rightarrow \infty$  after  $\omega \rightarrow \infty$

$$\therefore \lim_{\omega \rightarrow \infty} I_1 = 0$$

Similarly, putting  $1+\delta$  for  $\delta$  in this proof we can prove that  $\lim_{\omega \rightarrow \infty} I_2 = 0$

This proves the theorem I for  $p=0$ .

**2.3.** The proof of theorem I for  $p=n$  now follows by induction. Let us assume that the theorem is true for  $p=n-1$ . To prove the theorem for  $p=n$  we have to prove that,

$$(2.4) \quad \lim_{\omega \rightarrow \infty} \int_0^{\eta} \left[ \chi_{n+1+\delta}(\omega t) - \chi_{n+2+\delta}(\omega t) \right] dt = 0$$

$$\text{If } (2.5) \quad \frac{1}{t} \int_0^t \psi_n(u) du = O(1)$$

and

$$(2.6) \quad \frac{1}{t} \int_0^t |\psi_n(u)| du = O(1)$$

$$\text{Now } \lim_{\omega \rightarrow \infty} \int_{\delta}^{\eta} \chi_{n+1+\delta}(\omega t) dt = \lim_{\omega \rightarrow \infty} (n+1+\delta)(n+2+\delta) \omega \int_0^{\eta} \psi(t) \gamma'_{n+1+\delta}(\omega t) dt$$

On integrating by parts,

$$\begin{aligned} \lim_{\omega \rightarrow \infty} \int_0^{\eta} \chi_{n+1+\delta}(\omega t) dt &= \lim_{\omega \rightarrow \infty} (n+1+\delta)(n+2+\delta) \left[ \omega \psi_1(\eta) \eta \gamma'_{n+1+\delta}(\omega \eta) \right. \\ &\quad \left. - \omega^2 \int_0^{\eta} \psi_1(t) t \gamma''_{n+1+\delta}(\omega t) dt \right] \\ (2.7) &= \lim_{\omega \rightarrow \infty} -(n+1+\delta)(n+2+\delta) \omega^2 \int_0^{\eta} \psi_1(t) t \gamma''_{n+1+\delta}(\omega t) dt \quad \text{By (2.5)} \end{aligned}$$

Since  $t \gamma''_{n+1+\delta}(t) = (n+\delta) \gamma'_{n+\delta}(t) - (n+1+\delta) \gamma'_{n+1+\delta}(t)$ , (2.7) = 0 if

$$(2.8) \quad \lim_{\omega \rightarrow \infty} \omega \int_0^{\eta} \psi_1(t) \gamma'_{n+\delta}(\omega t) dt = 0$$

and

$$(2.9) \quad \lim_{\omega \rightarrow \infty} \omega \int_0^{\eta} \psi_1(t) \gamma'_{n+1+\delta}(\omega t) dt = 0$$

By the case of theorem I for  $p = n-1$ , (2.8) and (2.9) are satisfied if

$$\frac{1}{t} \int_0^t \psi_n(u) du = O(1)$$

$$\text{and } \frac{1}{t} \int_0^t |\psi_n(u)| du = O(1)$$

Therefore  $\lim_{\omega \rightarrow \infty} \int_0^{\eta} \chi_{n+1+\delta}(\omega t) dt = 0$

Putting  $\delta + 1$  for  $\delta$  in this proof we have

$$\lim_{\omega \rightarrow \infty} \int_0^{\eta} \chi_{n+2+\delta}(\omega t) dt = 0$$

Combining these results we have

$$\lim_{\omega \rightarrow \infty} \int_0^{\eta} \left[ \chi_{n+1+\delta}(\omega t) - \chi_{n+2+\delta}(\omega t) \right] dt = 0$$

This proves the theorem for  $p=n$ , where  $n$  is an integer.

(2.4) To prove the theorem for  $p=\alpha$ ,  $0 < \alpha < 1$ , we have to prove that

$$\lim_{\omega \rightarrow \infty} \int_0^{\eta} \left[ \chi_{\beta+1+\delta}(\omega t) - \chi_{2+\beta+\delta}(\omega t) \right] dt = 0 \text{ where } 1 > \beta > \alpha$$

This is a consequence of the following Lemma due to Verblunsky.<sup>1</sup>

Lemma 1. If  $\frac{1}{t} \int_0^t \psi_{\alpha}(u) du = 0$  (1)

and 
$$\frac{1}{t} \int_0^t |\psi_{\alpha}(u)| du = O(1)$$

Then 
$$\lim_{\omega \rightarrow \infty} \omega \int_0^{\eta} \psi(t) \gamma'_{1+\beta+\delta}(\omega t) dt = 0$$

For  $1 > \beta > \alpha > 0$ ,  $\delta$  being any arbitrary positive quantity.

2.5 Finally, the proof of theorem I for  $p=n+\alpha$ , where  $n$  is a positive integer again follows by induction.

This proves the theorem I completely.

We obtain as an immediate corollary.

**Theorem II.** The series allied with the derived Fourier series of an absolutely integrable (L) and periodic function,  $f(t)$  with period  $2\pi$ , is summable (C, K) to S at  $t=x$  for  $K > p+2$  if.

$$\frac{1}{t} \int_0^t \psi_{p+\delta}(u) du = 0 \quad (1)$$

and 
$$\frac{1}{t} \int_0^t |\psi_{p+\delta}(u)| du = O(1)$$

for all  $\delta > 0$ .



**3.1 Theorem III.** At a point at which

$$(3.1) \quad \frac{1}{t} \int_0^t |\psi_p(u)| du = O(1)$$

and for some integer  $r$

$$(3.2) \quad \lim_{t \rightarrow 0} \psi_r(t) = 0 \quad (1)$$

then (1.2) is summable (C, K) to S for  $k > p + 2$ .

This theorem follows from the theorem II and the following two lemmas which are due to Verblunsky<sup>2</sup>

Lemma 2. If  $\frac{1}{t} \int_0^t |\psi_p(u)| du = O(1)$

and  $\lim_{t \rightarrow 0} \psi_r(t) = 0 \quad (1)$

$r$  being a positive integer, then for all positive  $\delta$  we have

$$\frac{1}{t} \int_0^t \psi_{p+\delta}(u) du = 0 \quad (1)$$

Lemma 3. If  $\frac{1}{t} \int_0^t |\psi_p(u)| du = O(1)$

then  $\frac{1}{t} \int_0^t |\psi_{p+\delta}(u)| du = O(1)$

for all  $\delta > 0$ .

**3.2 Theorem IV.** At a point at which

$$(3.3) \quad \frac{1}{t} \int_0^t |\psi_p(u)| du = O(1)$$

a necessary and sufficient condition for the series (1.2) to be summable (C, K) for  $k > p + 2$  is that

$$(3.4) \quad \frac{1}{t} \int_0^t \psi_{p+\delta}(u) du = 0 \quad (1)$$

for all  $\delta > 0$ .

The condition is necessary because (3.4) holds by lemma 2, when (3.2) and (3.3) are satisfied, and when these are satisfied we have theorem III.

The condition is sufficient because the series (1.2) is summable for  $k > p + 2$  by theorem II and lemma 3, when (3.3) and (3.4) are satisfied.

Hence the theorem.

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# CHEMICAL EXAMINATION OF THE ESSENTIAL OIL OF *MENTHA ARVENSIS*

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## SUMMARY

1. Essential oil of Pudina, *Mentha arvensis* cultivated locally, collected by steam distilling the leaves and stem.
2. Physical chemical properties of the oil are given.
3. The oil has been chemically examined and found to contain 82% carvone and about 3.7% citronellol.

*Mentha arvensis* or Pudina as it is known in Bengali and Hindi is a small strongly scented herb belonging to the Natural Order of Labiatae. It is a cultivated garden plant and generally grows to a height of about 6—8 inches; the stems are erect and cluster-forming. It grows most abundantly during the hot and dry weather throughout the United Provinces, but during the rains the growth is very much stunted. The plant is very easily propagated by stem cuttings.

The herb is commonly sold almost throughout the year in the Indian vegetable markets for flavouring food materials and in the preparation of Chutneys. It is always available in bunches well soaked with water without which it gets blackened and spoilt. Sun-dried leaves are also available sometimes with Indian Apothecaries, but the aroma and medicinal properties of these are very much inferior to those of fresh leaves.

Although the leaves are widely used as a flavouring material, they are also used for medicinal purposes. The leaves are pounded wet, made into big tablets and dried in the sun. These tablets are used in stomach disorders in combination with other ingredients, generally salts and fried and powdered cumin seeds. The "Pudina water," obtained by distillation of the leaves in steam, is used against heat-stroke, fever and stomach troubles. The decoction of the leaves is sometimes administered in mild attacks of diarrhoea and cholera.

The medicinal properties of Pudina are apparently due to the essential oil contained in leaves which is of course responsible for their strong aroma and flavouring properties. It is well-known that several varieties of mint have already been examined by previous workers, the most important amongst them being *Menitha piperita* or ordinary peppermint, which contains a large proportion of

menthol (Parry<sup>1</sup>). Japanese *Mentha arvensis* has also been shown to contain an essential oil similar in properties to the oil derived from *Mentha piperita*. But the essential oils derived from *Mentha viridis*, *Mentha crispa*, *Mentha aquatica*, *Mentha canadensis* and *Mentha sylvestris* have been described in literature as "Spearment Oil," which differ from "Peppermint Oil" in having no menthol amongst their constituents. Although essential oils derived from *Mentha arvensis* grown in Japan, the United States of America, and Argentina have been examined by E. J. Parry, O. C. Garrent and Adolf Doering (Essential Oils and artificial perfumes, p. 215) (Analyst 1935, 319) (Abs. 1944, i 1172) respectively, yet no attempt appears to have been made to examine the essential oil from the Indian variety of the plant. This plant, though growing throughout India during most months of the year, seems to prosper in the United Provinces during the hot months of the year from April to June. It was, therefore, thought advisable to examine the essential oil from the plant cultivated in the United Provinces during the hot weather. A selected variety of the plant is grown by a local cultivator who sells huge quantities of the material in the market, and also supplies it to all the Hakims and Vaidas in the city for the preparation of indigenous medicines. It was from this source that the authors also obtained their supply of the raw material. A specimen of this plant was sent to the Botanical Survey of India, Calcutta, for identification and was reported to be *Mentha arvensis* Linn.

#### EXPERIMENTAL

Ten maunds of the fresh Pudina leaves obtained from the source mentioned above were steam-distilled in several instalments from a large copper still, tinned inside. The distillate was collected in big carboys wherein most of the essential oil collected at the top and was skimmed off. From the aqueous residue the rest of the oil was extracted with petroleum ether. The skimmed as well as the extracted oil was dried with anhydrous sodium sulphate and filtered. The physical and chemical properties of the pure essential oil were found to be as follows :—

TABLE I

The oil is transparent and deep green in colour. It becomes turbid at  $-2^{\circ}\text{C}$ , but does not congeal even on cooling upto  $-4^{\circ}\text{C}$ . The turbidity clears at  $16^{\circ}\text{C}$ .

1. Specific gravity	— 0.9403 at $15^{\circ}\text{C}$
2. Optical rotation	— $75.0^{\circ}$ at $33^{\circ}\text{C}$
3. Refractive index	— 1.4845 at $15^{\circ}\text{C}$
4. Acid value	— 1.0145
5. Ester value	— Nil
6. Saponification value	— Nil
7. Acetyl value	— Nil
8. Aldehyde (calculated as citral)	— 4.37%

The oil was submitted to fractional distillation under reduced pressure (66mm.) and the following fractions were collected.

TABLE II  
(Quantity of Oil taken = 123 Grams.)

Fractions	Temp. Range	Weight of Fraction
1	50—80°	1.8
2	80—100°	5.1
3	100—110°	4.9
4	110—115°	8.89
5	115—120°	5.71
6	120—140°	2.1
7	140—150°	2.8
8	155°	85.4
9	Residue	5.2

TABLE III  
*Physical Properties of the Fractions noted Above*

Fract. No.	Ref. Index	Sp. Gr.	Opt. Rot.
	15°	15°	40
1	1.4792	.9164	75°
2	1.4627	.8646	40
3	1.4487	.8141	55
4	1.4357	.7813	...
5	1.4267	.7715	45
6	1.4832	.9204	20
7	1.4852	.9286	—60
8	1.4952	.9727	—25
9	1.5107	...	...

Fraction Nos. 1, 2, 6, 7 and 8 were mixed together and distilled a number of times at the ordinary pressure with a Young's Still head having four bulbs; the following main fractions were collected.

TABLE IV  
(Total Quantity taken—62 Grams.)

Fraction No.	Boiling range (°C)	Weight of the fraction (Gm.)
10	Below 150	6.85
11	150—200	3.92
12	200—201	0.7
13	201—202	8.37
14	205	3.69
15	222	2.4
16	222—223	28.75
17	224—230	1.2
18	Residue	4.45

TABLE V  
*Physical Properties of the Above Fractions*

Fraction No.	Refractive Index	Sp. Gr.	Optical Rotation at 40°C.
	15°C	15°C	
10	1.477	0.7150	plus 60
11	1.485	0.8579	plus 100
12	1.497	...	...
13	1.496	0.9502	...
14	1.497	0.9447	plus 25
15	1.490	0.9502	...
16	1.494	0.9612	plus 75
17	1.501	1.0135	...

Fraction No. 8 was identified to be d-carvone. The oxime, prepared in the usual manner on recrystallization from alcohol, melted at 74°C. The semi-carbazone melted at 162°C. The bisulphite compound was prepared by shaking a little of the fraction with a saturated solution of sodium bisulphite. It was recrystallized from boiling water in glistening white laminæ. The hydrogen sulphide addition product was obtained by passing the gas through an ice cold solution of 20 parts of the substance in 5 parts of alcohol and one part liquor ammonia. It crystallized out from the solution in colourless glistening spangles. On qualitative examination carvone was found to be present in almost all the fractions, and fractions Nos. 1 and 8 were quantitatively estimated for carvone. In fraction No. 1 it was found to be =2.42 per cent. and in fraction No. 8 =80.0 per cent. The original oil was also

estimated and found to contain 82.2 per cent. of carvone. (Carvone<sup>2</sup> was estimated by preparing its semi-carbazone according to the method recommended by Analyst (1927, 52, 53).

Fraction No. 3, which was not apparently much contaminated with carvone, was identified to be d-citronellol. It yielded a liquid oxime and a semi-carbazone crystallizing in glistening flakes melting at 83-84°C.

The residue of distillation was examined, but did not yield any solid substance of the nature of stearoptene or wax.

Fractions Nos. 10 and 11 were found to give colour reaction with acetic anhydride and sulphuric acid, and therefore contained carene

All other fractions gave tests for carvone only.

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# MIGRATION OF PARA HALOGEN ATOM IN A DERIVATIVE OF META-CRESOL, PART II

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## SUMMARY

1. Nitration of 4-bromo-3-methylphenol with the theoretical quantity of Nitric acid under ice cooling gives rise to two Mono-nitro-bromo-Methylphenols.
2. The two Mono-nitro-bromo-Methylphenols have been separated by steam distillation and their quantities have been estimated roughly.
3. The volatile portion constituting about 30 per cent. of the total nitrated product M. P.  $124^{\circ}\text{C}$ , has been identified to be 4-bromo-6-nitro-3-methylphenol and on further nitration forms a dinitro-bromo-Methylphenol M.P.  $78^{\circ}\text{C}$  which has been identified as 4-bromo-2,6-dinitro-3-methylphenol.
4. The non-volatile portion is an oily liquid, constituting about 70 per cent. of the total nitrated product, and on further nitration] forms a dinitro-bromo-Methylphenol M. P.  $115^{\circ}\text{C}$ , identical with 2-bromo-4,6-dinitro-3-methylphenol.
5. The constitution of the dinitro compound formed by the nitration of 1-chloro-4-bromo-3-methylbenzene has been established as 1-chloro-4-bromo-2,6-dinitro-3-methylbenzene.
6. 4-bromo-2,6-dinitro-3-methylphenol has been synthesised from 1-chloro-4-bromo-2,6-dinitro-3-methylbenzene by application of Borsche's method.

In a previous communication (Proc. Nat. Acad. Sc. Vol. 9, Pt. 2, pp. 89—92, May, 1939), it has been shown, that on nitration of 4-bromo-3-methylphenol, the bromine atom migrates from the para to the ortho position, and the constitution of the dinitro-bromo-cresol so formed is 2-bromo-4,6-dinitro-3-methylphenol and not 4-bromo-2,6-dinitro-3-methylphenol as assigned by Walther and Demmelmeyer (J. Pr. Chem. 92, 123). In the present paper we have studied this reaction more closely, in order to find out whether the bromine atom migrates even under milder conditions of nitration. We have also established the constitution of the dinitro-bromo meta-cresol m. p.  $78^{\circ}\text{C}$ , obtained by Gibbs and Robertson (J. C. S., 1914, 1891) and also by Raiford and Leavel (J. A. C. S., 36, 1505), by synthesising it from 2,6-dinitro-4-bromo-1-chloro-3-methylbenzene.

Meldola and Streatfield (J. C. S., 1890, 691) have studied the action of nitric acid on para-bromo-phenol, and have shown that on bromination of phenol both



ortho and para-bromo compounds are formed, which can be separated by nitrating the mixture and then submitting it to steam distillation. By this operation the para-bromo-nitro compound is distilled off, leaving the ortho-bromo-nitro compound in the flask. This method was actually employed by them to estimate roughly the amounts of ortho and para-bromo-phenols on bromination of phenol.

A slight modification of this method may be utilized to determine the extent of migration, when a halogenated phenol is nitrated. Starting with the purest sample of a para-halogenated-phenol, if it is found that after nitration two mono-nitro-bromo compounds have been formed, one being volatile in steam and the other non-volatile; then by estimating the amounts of these two mono-nitro-bromo compounds one can calculate roughly the extent of migration of the halogen atom, as the formation of an ortho-bromo-nitro compound can only be ascribed to the migration of the halogen atom.

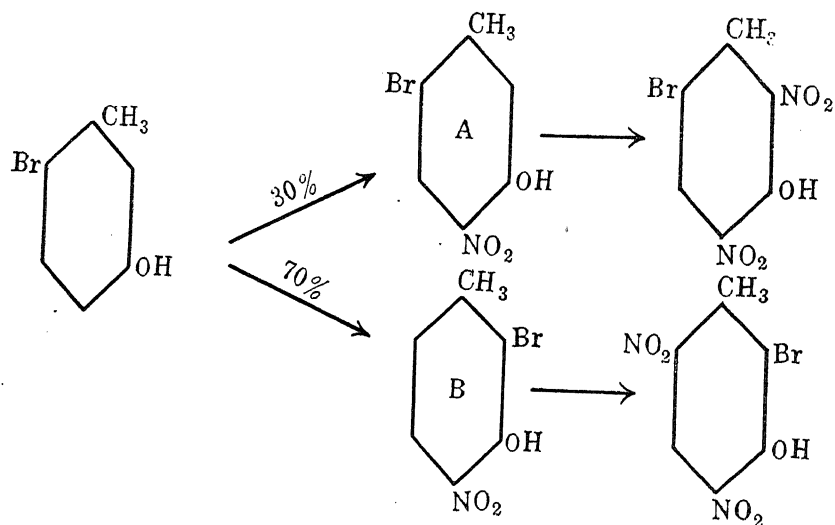
This method was therefore applied to 4-bromo 3-methylphenol, in order to determine whether migration of the bromine atom takes place even on mono-nitration. The purest sample of 4-bromo 3-methylphenol prepared by Darzens and Levys method (C. C., 4A, 2319) was nitrated with the theoretical quantity of nitric acid, under cooling, as mentioned by Walther and Zipper (J. Pr. Chem., 91, 376). After an hour some crystals separated out, which, however, were not filtered and instead the whole thing was diluted with ice-water and then steam-distilled. About 30 per cent. of the nitrated product distilled off leaving about 70 per cent. in the flask. The volatile portion melted at 124°C and was found to be identical with 4-bromo 6-nitro 3-methylphenol obtained by the bromination of 6-nitro 3-methylphenol (Gibbs and Robertson, J. C. S., 1914, 1885), as the corresponding acetyl and toluene-sulphonyl derivatives obtained from these two compounds are identical.

This mono-nitro compound m. p. 124°C, on further nitration gives a dinitro-bromo compound m. p. 78°C and which was found to be identical with the dinitro-bromo compounds obtained by Gibbs and Robertson (1914, J. C. S., 1885) and also by Raiford and Leavel (J. A. C. S., 36, 1505), which, as has been shown subsequently, has the constitution 2, 6-dinitro 4-bromo 3-methylphenol.

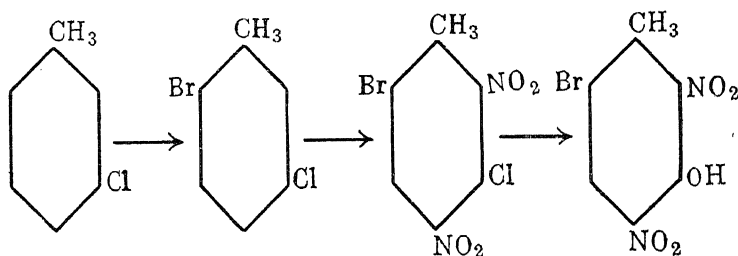
The non-volatile portion left in the flask after steam distillation is the ortho-bromo-nitro compound, and as such, it is obvious that the bromine atom migrates even on mono-nitration of 4-bromo 3-methylphenol. This mono-nitro compound left in the flask on further nitration gave a dinitro-bromo compound m. p. 115°C identical with 2-bromo 4, 6-dinitro 3-methylphenol.

To sum up, it may be said that on nitration of 4-bromo 3-methylphenol, migration of the bromine atom takes place forming a large quantity of ortho-bromo-nitro compound with a little of the para-bromo-nitro compound which on further nitration yields mainly 2-bromo 4, 6-dinitro 3-methylphenol.

The course of the reaction may be represented thus :—



With excess of nitric acid the course of the reaction is mostly towards B, and hence, in the final product we get mostly 2-bromo 4, 6-dinitro 3-methylphenol. Lastly, we established the constitution of the dinitro-bromo-cresol m. p.  $78^{\circ}\text{C}$  by synthesising it from meta-chloro-toluene as follows :—



This dinitro-bromo-cresol was found to be identical with those prepared by Gibbs and Robertson, and Raiford and Leavel, as the corresponding acetyl and para-toluene-sulphonyl ester were also found to be identical.

#### EXPERIMENTAL

*Nitration of 4-bromo 3-methylphenol:* 4-bromo 3-methylphenol prepared by Darzens and Levys method was further purified by recrystallising once more with alcohol and leaving it on the porous tile. 20 gms. of this dry material m. p.  $60^{\circ}\text{C}$  was dissolved in acetic acid and the calculated quantity of nitric acid, added drop by drop, under constant stirring, the mixture being cooled with ice. It was allowed to stand

for an hour when some crystals separated out. This was, however, not filtered and instead the whole mixture was diluted with ice-water and then steam-distilled. The portion which was volatile weighed about 7 gms. (30%), and melted at 124°C, rest (70%) being non-volatile was left in the flask.

*6-nitro 4-bromo 3-methylphenol*: This compound was obtained by the bromination of 6-nitro 3-methylphenol, and was found to be identical with the compound which was volatile in steam, and melted at 124°C as the acetyl, toluene-sulphonyl and the dinitro derivatives of these two compounds were also found to be identical.

*Acetyl derivative* was obtained in the usual way, by heating 6-nitro 4-bromo 3-methylphenol with acetic anhydride and anhydrous sodium acetate, m. p. 58°C.

Found Nitrogen—5.0%. Required Nitrogen—5.1%.

*Para-toluene-sulphonate of 6-nitro 4-bromo 3-methylphenol*: This was obtained in the usual way, by suspending calculated quantities of the phenol and para-toluene-sulphonyl chloride in hot water and adding sodium carbonate little by little until further addition produced no more coloration and then treating in the usual way—m. p. of the ester is 95°C. It is also obtained by using diethylaniline instead of sodium carbonate, as the condensing reagent. Found S.—8.3%. Required S.—8.27%.

*Nitration of the volatile portion*: The compound m. p. 124°C was dissolved in acetic acid and an excess of concentrated nitric acid added. After some time the whole thing was diluted with water and the mass that separated out was recrystallised from alcohol, m. p. of this dinitro compound is 78°C. This was found to be identical with Gibbs and Robertson and Raiford and Leavel's dinitro-bromocresol.

*Nitration of the non-volatile portion*: The non-volatile portion left in the flask, after steam distillation of the product, obtained by nitration of 4-bromo 3-methylphenol, constituted about 70% of the total product. This portion was separated and on further nitration in acetic acid solution gave a dinitro compound m. p. 115°C. This was identified to be 2-bromo 4, 6-dinitro 3-methylphenol.

*4-bromo 2, 6-dinitro 3-methylphenol*: This compound was obtained by several methods:—

(a) by the nitration of 6-nitro 4-bromo 3-methylphenol in acetic acid solution (Gibbs and Robertson J. C. S., 1914, 1891) —

(b) by the nitration of 6-nitro 4-bromo 3-methylphenol in sulphuric acid (Raiford and Leavel: J. A. C. S., 36, 1505)—

(c) from 6-bromo metacresotinic acid, by nitrating it in acetic acid solution—

(d) from meta-chlorotoluene—m. p. of all these compounds is 78°C.

*Synthesis of 4-bromo 2, 6-dinitro 3-methylphenol from metachlorotoluene*: Meta-chlorotoluene was brominated in  $\text{CCl}_4$  solution using aluminium mercury couple as a catalyst, (J. C. S., 1914, 1910). The chloro-bromo-toluene formed has the constitution 4-bromo 1-chloro 3-methylbenzene—this was then nitrated with a

mixture of concentrated sulphuric acid and fuming nitric acid in equal portions (J. C. S., 1914, 1912). On pouring this mixture in water a solid mass separated out which was recrystallized twice from methyl alcohol—m. p. 112°C.

*Constitution of X. X. dinitro 4-bromo 1-chloro 3-methylbenzene:* The above dinitro compound has not been assigned any constitution so far. We have been able to fix up its constitution as 4-bromo 1-chloro 2, 6-dinitro 3-methylbenzene. The constitution has been based upon the fact that when 1: 4 dibromo or 1: 4 dichloro 3-methylbenzene is nitrated by the same method, then the dinitro compound that is formed has the constitution 1: 4 dibromo 2, 6-dinitro 3-methylbenzene or 1: 4 dichloro 2: 6-dinitro 3-methylbenzene. From analogy, therefore, on nitration of 1-chloro 4-bromo 3-methylbenzene we should get a 2: 6-dinitro compound. This was further confirmed by the fact, that on treatment of this dinitro compound with aniline, an anilide was obtained m. p. 116°C corresponding to 4-bromo 2, 6-dinitro 3-methyl-1-phenylamine; which has been obtained previously by the action of aniline on 1, 4-dibromo 2, 6-dinitro 3-methylbenzene.

*4-bromo 2, 6-dinitro 3-methylphenol from 4-bromo 1-chloro 2, 6-dinitro 3-methylbenzene by the application of Borsche's method:*—7.4 gms. of 4-bromo 1-chloro 2, 6-dinitro 3-methylbenzene, 7.4 gms. sodium acetate and 22.2 gms. of acetamide were heated in a flask at 180°C, in an oil bath for an hour. The fused mass was then cooled and treated with 40 c. c. aqueous ammonia and then boiled with a little animal charcoal, filtered and the filtrate acidified with nitric acid. The solid mass on several recrystallisations from alcohol melted at 78°C. Yield is very poor.

*P-Toluene-sulphonyl-ester of 2, 6-dinitro 4-bromo 3-methylphenol* was obtained in the usual way by heating calculated quantities of the phenol and para-toluene-sulphonyl chloride in water and then adding sodium carbonate little by little, until further addition produces no more coloration. The mass that separated out on cooling was filtered, washed with water and finally recrystallised from acetic acid, m. p. 128°C.

The same ester was obtained by using diethylaniline as the condensing reagent. Found S. — 7.5 per cent, 7.3 per cent. Required S. — 7.4 per cent.

*Acetyl derivative of 2, 6-dinitro 4-bromo 3-methylphenol:*—This was obtained in the usual way by heating the phenol with acetic anhydride and fused sodium acetate, colourless crystals from acetic acid, m. p. 121°C.

Found N. — 8.8 per cent. Required N. — 9.2 per cent.

My special thanks are due to the Lucknow University, for the facilities offered for research, and to Dr. S. M. Sane for help and guidance during the course of the work.

# COMPOSITION OF PATENT STILL MOLASSES FUSEL OIL OF INDIAN ORIGIN. PART III

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(Received on April 15, 1940)

## SUMMARY

Indian molasses fusel oil obtained from the Patent Still Distillery of Messrs. Muree Brewery Co. Ltd. of Rawalpindi, Punjab, was exhaustively examined and fractionally distilled hundreds of times, whereby it was resolved into the following constituents: butyric aldehyde, ethyl alcohol, isopropyl alcohol, isopropyl acetate, n-propyl alcohol, water, acetal, ethyl isobutyrate, isobutyl alcohol, n-butyl alcohol, isobutyl acetate, n-butyl acetate, isoamyl alcohol, n-amyl alcohol, n-hexyl alcohol, n-heptyl alcohol, n-octyl alcohol, n-nonyl alcohol, furfural and a number of high boiling esters of ethyl, isoamyl, n-amyl and n-octyl alcohols in combination with valeric, octylic, pelargonic and capric acids. The non-volatile residue obtained at the end of the distillation was found to be a soft wax consisting of esters of lauric, myristic, palmitic, oleic and stearic acids with mainly n-octyl alcohol. The wax which separated out from the fusel oil on removal of the light fractions on distillation, melted at 125-126°C on repeated crystallisation from absolute alcohol and was found to be an ester of lauric acid with some unknown alcohol.

In two previous communications by the present author<sup>1,2</sup>, molasses fusel oil obtained from the Patent Still Distilleries of Messrs. Carew and Co. Ltd. of Shah-jahanpur and of Messrs. Begg Sutherland and Co. Ltd. of Cawnpore were submitted to intensive fractional distillations with the help of special fractionating columns and ultimately separated into a large number of constituents consisting mainly of alcohols and esters. In the present communication, molasses fusel oil obtained from an altogether different source, that is, from the Patent Still Distillery of Messrs. Muree Brewery Co. Ltd. of Rawalpindi (Punjab) was taken for examination. This fusel oil was found to be quite similar to the Cawnpore fusel oil in physical properties and also chemical composition, the only notable exception being the presence in the former of comparatively large proportions of butyric aldehyde. The presence of this aldehyde also gave to the Rawalpindi fusel oil a characteristic note of odour which was different from that of any other fusel oil previously examined. The fusel oil also contained a comparatively large proportion of waxy matter in solution, which partially separated out from the oil on allowing it to stand for some time, the complete separation being effected on the removal of the low-boiling fractions by distillation. This wax was found to be different from that obtained from Cawnpore fusel oil.

Compared to Cawnpore fusel oil which contains 4 per cent. of high-boiling constituents, Rawalpindi fusel oil contains much less of these materials, that is, only about 1·8 per cent. Whereas Cawnpore fusel oil contains 85 per cent. of isoamyl alcohol, Rawalpindi fusel oil contains 73 per cent. of this substance. With the exception of these minor differences, the two fusel oils are quite similar to each other in most respects. From the commercial point of view, Rawalpindi fusel oil would be a valuable source of isoamyl alcohol for the manufacture of its acetic ester and also for use as a solvent.

#### EXPERIMENTAL

The fusel oil was obtained through the courtesy of Messrs. Muree Brewery Co. Ltd. of Rawalpindi (Punjab) from their Patent Still Distillery using molasses as raw material. As the company does not recover the fusel oil but allows it to go to waste, a special receptacle had to be placed for this occasion to the waste pipe, in order to collect a quantity of this material. On arrival at Allahabad, it was found to be a turbid liquid containing a large proportion of water in suspension. The whole thing was allowed to stand in a cool place for about a week, when the water completely separated and settled as a bottom layer. The clear supernatant fusel oil was siphoned off and from 4 gallons of the crude fusel oil, 10930 c.c. of the water-free oil was obtained and submitted to fractional distillation.

The Rawalpindi fusel oil was found to be a clear bright yellow oil with a characteristic odour and a specific gravity of 0·8414 at 25°C. The fractional distillation of this substance was effected as described in Part II of these series of investigations, utilising the identical distillation apparatus. After hundreds of distillations involving tedious and complicated experimental technique, the fusel oil was resolved into 28 fractions, each boiling within very close range, and most of which have been identified by formation of derivatives or by some other suitable means. The complete result of analyses is given in a tabular form for the sake of abbreviation, and is shown in Table I below.

TABLE I

<i>Complete analysis of Rawalpindi fusel oil</i>					<i>Light fractions.</i>
Total quantity taken=10930 c.c.					
Fraction No.	Boiling range (°C)	Correct B. P. (°C)	Quantity (c.c)	Per cent. in fusel oil	Main composition
1	70-75	73-74	112	1·0	Butyric aldehyde
2	75-80	73-74	634	5·8	Butyric aldehyde (containing about 8% ethyl alcohol)

Fraction No.	Boiling range (°C)	Correct B. P. (°C)	Quantity (c.c.)	Per cent. in fusel oil	Main composition
3	80-85	83	211	2.0	Isopropyl alcohol
4	85-90	88-90	72	0.7	Azeotropic mixture (75% isopropyl alcohol + 25% isoamyl alcohol)
5	90-95	91	2	0.02	Isopropyl acetate
6	95-99	97	9	0.08	n-propyl alcohol
7	100	100	664	6.0	Water
<i>Medium fractions</i>					
8	100-105	104	4	0.04	Acetal
9	105-110	108	2	0.02	Isobutyl alcohol
10	110-115	110	4	0.04	Ethyl isobutyrate
11	115-120	116	7	0.06	n-butyl alcohol + iso-butyl acetate
12	120-128	126	20	0.2	n-butyl acetate
13	128-131	129-131	7968	72.9	Isoamyl alcohol
14	133-140	137	9	0.08	n-amyl alcohol
15	140-150	145	2	0.02	Ethyl valerianate
<i>Heavy fractions</i>					
16	150-160	157	8	0.08	n-hexyl alcohol
17	160-170	163	3	0.03	Furfural
18	170-180	174	3	0.03	n-heptyl alcohol
19	180-190	...	1	0.01	Unidentified
20	190-200	197	6	0.05	n-octyl alcohol
21	200-210	205	14	0.13	n-amyl-n-valerate
22	210-220	214	37	0.24	n-Nonyl alcohol
23	220-230	227	105	1.0	Ethyl pelargonate
24	230-240	239-240	17	0.16	Ethyl caprate
25	240-250	248	112	1.0	Isoamyl-n-octylate
26	250-260	259	146	1.33	Isoamyl pelargonate
27	260-270	266	31	0.23	n-amyl pelargonate
28	270-280	278	11	0.1	Isoamyl caprate
29	280-290	...	6	0.05	Unidentified
30	290-300	...	4	0.04	Unidentified
31	300-310	...	4	0.04	Unidentified
32	Residue (waxy)	...	97	0.88	

The above waxy residue was found to have a composition similar to that obtained from Cawnpore fusel oil (Cf. Dutt<sup>2</sup>).

The cream-coloured waxy matters that had separated out from the original fusel oil on standing and also after the removal of the light fractions on distillation, were combined together and crystallised from alcohol with the addition of animal charcoal and was obtained in the form of large rectangular plate with fatty lustre, and melting at 125-126°C. The substance was found to be different from the wax obtained from Cownpore fusel oil (M. P. 121°C). The total quantity obtained was 3.5 grams. On hydrolysis with alcoholic Caustic potash, it gave lauric acid.

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# PHYSIOLOGICAL STUDIES ON THE WHEAT PLANT, PART I— THE EFFECT OF MANURES ON THE TOTAL NITROGEN AND AMINO-ACID NITROGEN IN *TRITICUM* *VULGARE* AND SOIL

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## SUMMARY

1. The total nitrogen and the amino-acid nitrogen in the wheat plant is related to the total nitrogen contents of the soil. The nitrogen contents of the latter descends in the order compost bed, unmanured garden soil, molassed sub-soil and sub-soil and so does the nitrogen contents of the wheat plant growing in these successive soils.

2. During the 1st phase of the ontogenic drift the amino-acid nitrogen shows a parabolic curve of the type  $x^2 = 4 \times 11088y$ . This phase starts with the seedling stage and ends at the metabolic maturity when the amino-acid contents are the lowest and conversely the total nitrogen the highest.

3. In the 2nd phase which is the presenescent phase and which just precedes the formation of the ears, the contents of the amino-acid nitrogen again rises and the total nitrogen falls. This has been ascribed to the needs of the young grain for proteins and it is in the mobile amino-acid nitrogen form that the proteins travel towards the ears.

## INTRODUCTION

According to Waksman<sup>9</sup> nitrogen in the "stable manure" is excreted by different animals, in the following relative amounts:—

Nature of animals.	Cow.	Ox.	Horse.
Per cent of the nitrogen consumed .. ...	100	100	100
Found in the solid matter .. ...	47.5	33.9	32.4
Found in the urine ... ..	31.0	54.8	60.7

About half of the nitrogen found in fresh manure is in the form of ammonia and urea, while the other half is in the form of proteins and other complex organic nitrogenous compounds. The importance of the "stable manure" in soil process has been variously ascribed to 4 distinct factors:—

1. Manure offers a readily available supply of nitrogen, phosphoric acid and potash for the growth of higher plants.

2. Since manure undergoes rapid decomposition in the soil, it is a good source of carbon dioxide, necessary for plant growth.
3. The organic matter of the manure serves the purpose of replenishing the supply of humus in the soil.
4. Manure exerts a favourable influence upon the soil microbiological activities.

The "artificial manures", like molasses on the other hand, supplies energy as they contain a large percentage of carbohydrate. According to Waksman, a number of microbiological processes are brought about, when molasses is used as a source of energy, those include possibly non-symbiotic fixation of nitrogen. On the other hand, Dhar<sup>1</sup> and his co-workers believe that the oxidation of the carbohydrates added to the soil with the molasses sets free energy, which is utilized in the combination of atmospheric nitrogen and oxygen present in the soil leading to the formation of nitrates. The inorganic manures, specially potassium nitrates not only supplies nitrogen, but also favours the development of *Azotobacter*, fixing the atmospheric nitrogen indirectly.

The present work, which is a part of the larger work on the wheat plant, was undertaken with a view to find the amino-acid nitrogen/total nitrogen ratio through the ontogenic drift of the plant growing in diverse soils containing molasses and farm-yard manure. The 2nd part, which is a logical continuation of this work, is published separately and deals with *in-vitro* experiments on the effect of molasses on the soil nitrogen in both light and darkness.

#### MATERIAL AND TECHNIC

##### A. *Material.*

Samples of wheat plants and soils were obtained from the experimental plots in the Botanical Garden. In all, there were 4 plots arranged in two rows. Each plot measured 19'×11' and was lined with bricks, so that contamination from neighbouring fields was prevented. The surface soil of two plots were replaced by sub-soil, got from a depth of 2 ft. and below. One of them was treated with molasses and the other was left unmanured as the control bed. Of the other two plots, both contained surface soil but one of them was treated with farm-yard manure and the other served as the corresponding control.

Seeds were also sown in pure sawdust in large pots and these seedlings were analysed. All the plants were raised from the strain Pusa 52.

##### B. *Sampling.*

The technic employed in sampling the leaves, closely follows the methods of Maskell and Mason<sup>5</sup> (1929) and Petrie and Wood<sup>6</sup> (1938). Each leaf sample

consisted of about 30 mature and healthy leaves of nearly the same age, and were cut for experimental work between 9 and 10 a.m. each time.

The procedure for sampling the soil was by randomization. The soil samples were collected on the same days and time on which the leaf samples were collected. Each soil sample was well-dried in air in an electric oven at a constant temperature of 60°C. It was then powdered, mixed and sieved through 1 m.m. mesh.

### C. *Method of Analysis.*

(a) *Leaf*:—5 grams of fresh and healthy leaves were quickly weighed, cut into small pieces and dropped into boiling distilled water and boiled for a short time. The material was then finely crushed with purified sand in a hand mortar and boiled again. It was filtered and the residue was washed several times with hot distilled water. The filtrate was concentrated to 25 c.c.

For the estimation of amino-acid nitrogen of the leaf, the above filtrate was treated with 1 c.c. of 10 per cent. acetic acid and the precipitate obtained was added to the residue. The filtrate was analysed for amino-acid by the modified Van Slyke's method. The apparatus had to be modified when the amount of amino-acid nitrogen was very small. The gas burette was replaced by a microburette with an outer glass jacket in which the temperature of the water was kept constant at 30°C.

The residue, from which the amino-acid was removed, by the previous procedure, was digested according to the modified Kjeldahl method of Robinson, McLean and Williams<sup>7</sup> (1929). The ammonium sulphate formed by this method was estimated colorimetrically by Nessler's reagent using Hellige colorimeter.

(b) *Soil*:—The total nitrogen of the soil was estimated by the "wet digestion" method of Srinivasan<sup>8</sup> (1932) by allowing 5 grams of dry powdered and sieved soil with 20 c.c. distilled water and 20 c.c. concentrated  $H_2SO_4$ , to stand over-night and then estimating nitrogen by the modified Kjeldahl's method using Nessler's reagent.

### D. *Expression of Results.*

In all the experiments, "fresh weight" method has been employed in the case of leaves.

In the case of soils the results are expressed on the air "dry weight" basis in every experiment.

## OBSERVATIONS

### A. *Amino-acid Nitrogen of the Wheat Plant.*

The estimation of amino-acid nitrogen in the leaves was started when the seedlings were 5—7 days old and continued at periodical intervals till the grains were formed and the leaves had begun to dry.

As has been said before, the seeds were sown in 4 plots, *viz.*, molasses bed, compost bed, garden soil bed (unmanured) and sub-soil bed (unmanured). The results are plotted graphically in Fig. 1. The amino-acid nitrogen in gram per 100 gm. of fresh leaves shows that in all the 4 cases the quantity of amino-acid nitrogen in the seedling stage is about .04 gm. per cent.

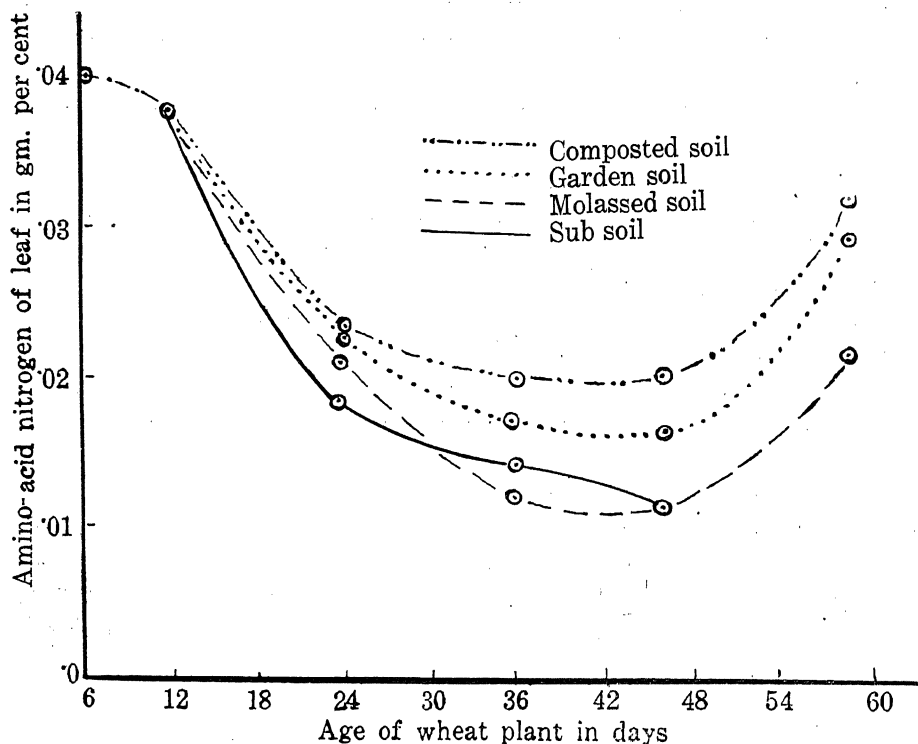


Fig. 1

As the seedlings advance in age the nitrogen rapidly falls for 25 days. Thereafter the fall slows down till the 46th day. The course of the fall varies according to the plot in which the seedling had been growing, the course descending in the order compost bed, unmanured garden soil, molassed sub-soil and unmanured sub-soil. At the end of 46 days the lowest amount of amino-acid nitrogen noted was for the leaves from the molassed sub-soil and the highest value was attained in the composted garden soil bed.

The amino-acid nitrogen rises again from the 46th day to the 58th day in all the cases; but unlike the fall, where the ratio varied according to the plot, the rise in amino-acid nitrogen from the lowest point, is the same in all the 3 cases, *viz.*,

- (1) Compost bed, from  $\cdot 0200$  gm. to  $\cdot 0315$  gm. =  $+\cdot 0115$  gm.
- (2) Garden soil „  $\cdot 0160$  gm. to  $\cdot 0291$  gm. =  $+\cdot 0131$  gm.
- (3) Molasses „  $\cdot 0110$  gm. to  $\cdot 0213$  gm. =  $+\cdot 0103$  gm.

These slight differences in the quantity are within the limits of experimental error.

#### B. Total Nitrogen of the Wheat Plant.

Variation in the total nitrogen contents of leaves, from the seedling to the fruiting stage shows the same type of curve as in the case of the amino-acid nitrogen. At the seedling stage the quantity is high which rapidly diminishes and then rises again, Fig. 2. But the rate of fall of the total nitrogen is much faster than that of the amino-acid nitrogen and the minimum is reached in 12 days as opposed to 46 days for the amino-acid nitrogen.

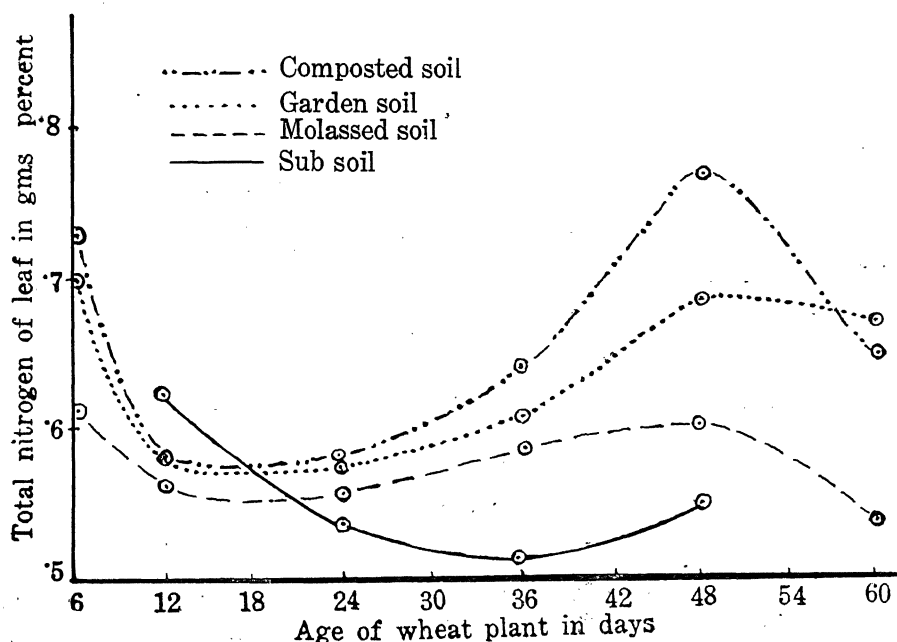


Fig. 2

The peak value for total nitrogen is reached at the end of 48 days in all the cases. This is in contrast to the amino-acid nitrogen which is the lowest at this period (See Fig. 1). Having reached this peak value, total nitrogen again shows a distinct fall.

C. *Total Nitrogen of the Dry Soil.*

The total nitrogen of the composted soil, garden soil, molassed soil and the sub-soil, is shown graphically in Fig. 3. The total nitrogen of the composted bed at

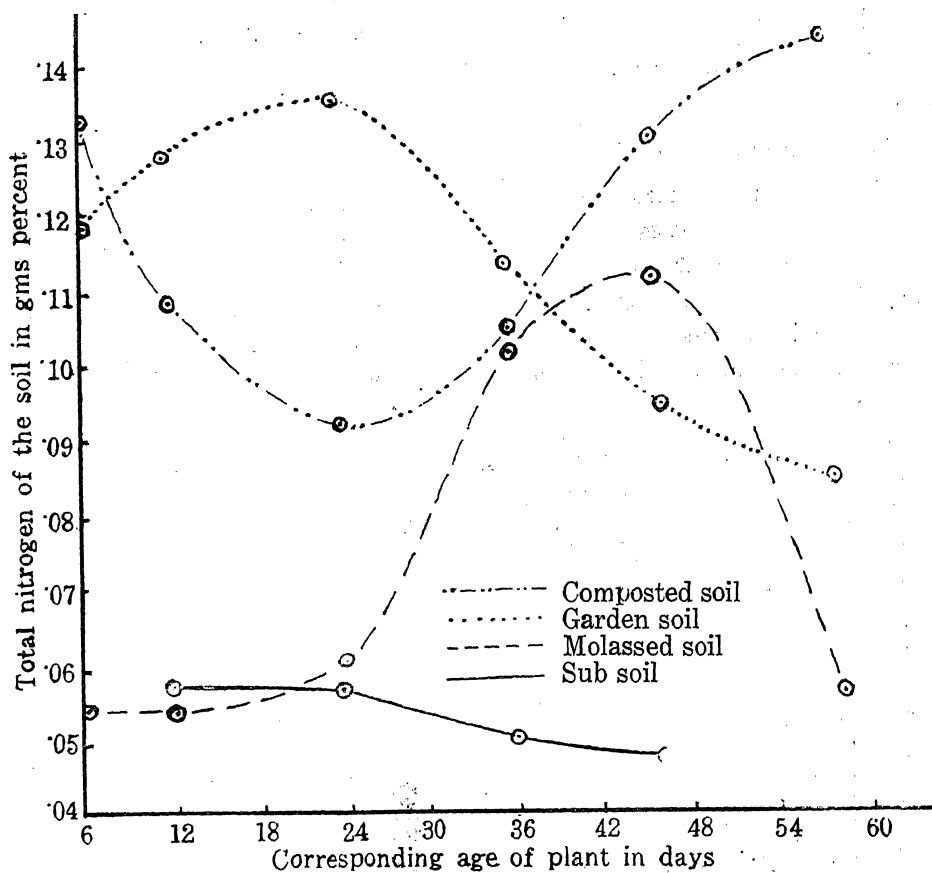


Fig. 3

the start of the experiment is about 0.13 gm. per 100 gm. of the dry soil, but after about 25 days the quantity of total nitrogen falls to a minimum of 0.09, thereafter it rises again steadily to reach 0.14 gm. The unmanured garden soil on the contrary shows a slight rise for the first 25 days and then a steady decline.

The value of total nitrogen for both the molassed bed and the sub-soil is near about 0.055 gm. %. But whereas there is a steady fall with time in the nitrogen value for the sub-soil, it rises steadily for about 46 days, in the molassed bed and then falls off.

*D. Nitrogen Contents of the Grain.*

When the plants were about two months old, they were characterised by swollen stems. These were due to the presence of young ears inside the sheathing leaves. By a longitudinal slit with a sharp knife, at this region, the young ears bearing milky grains were taken out and analysed. The result of the analysis is given in Table I:—

TABLE I

Nitrogen contents in grm. per 100 grm. of the grain.

Samples from	Amino-acid nitrogen	Total nitrogen.
Molasses bed ... ..	·045	·464
Compost bed ... ..	·053	·422
Garden soil (unmanured) ...	·050	·421

It is evident from the table that the total nitrogen of the ear from the compost bed and the unmanured garden soil is about the same, but there is a slight increase in the case of the molasses bed. The amino-acid nitrogen on the other hand, is slightly more for compost bed and garden soil than for molasses bed.

## DISCUSSION OF THE RESULTS

*A. The Amino-acid Nitrogen.*

The relation between age and amino-acid nitrogen may be formulated somewhat as follows. Every seedling during its ontogenic drift starts with a relatively high percentage of amino-acid nitrogen, which falls rapidly with metabolic maturity. At about the time the life cycle of the plant is half completed, the amino-acid nitrogen is at its lowest value. This is the peak of the metabolic maturity of the leaves and marks the end of the first phase in its ontogenic drift. The second phase, which follows, could be called the presenescent phase and is the fruiting stage. In this stage amino-acid nitrogen again rapidly rises. The fall in the amino-acid nitrogen in the first phase for the plants in all the beds may be schematically shown by Fig. 4.

This is more or less the type of parabolic curve. Observations of the seedlings growing in various beds show the same typical drift, though at slightly different rates, since the amino-acid nitrogen values differ according to the manurial values of the soil. The mathematical calculations give the following values for the plant growing in the farmyard manure soil.

Plotting a graph of the following

Days.	Amino-acid nitrogen per cent.
6	·040
12	·037
24	·023
36	·020

We take the origin at (6, .00) and get the points plotted near about the curve  $x^2 = 4 \times 11088y$ , a parabola which passes through three of the points and is only a little further away from the point (12, .037) marked  $x$  in Fig. 4.

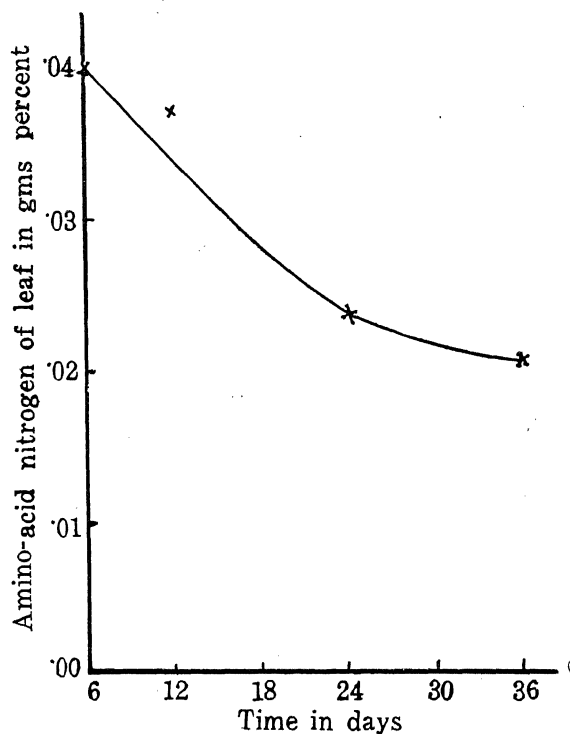


Fig. 4

#### B. The Total Nitrogen.

The initial total nitrogen value of the plants in the 4 different plots, may be resolved into 2 groups: (1) The compost group and (2) the sub-soil group. The similarity of the amount of total nitrogen in the leaves of the plants growing in the first group may be due to the excess of nitrogen in the form of nitrates present in both the compost and garden soil beds as is evident from Fig 3. While the low values of total nitrogen in the sub-soil and molasses beds may be due to the paucity of nitrates in these beds at the commencement of the experiments. Due to the nitrates and such other forms of nitrogen in the soils containing molasses and farmyard manures, the total nitrogen towards the latter half of the life cycle of plants growing in these soils get greatly augmented. This increase is greatly marked in the case of the plants growing in compost bed than those growing in molasses bed. That there is undoubtedly a marked influence of



the total nitrogen of the soil on the total nitrogen of the plant is evident by the comparison of Figs. 2 and 3. There is a very close parallel indeed in the case of the molassed bed and the plant growing on it, while for other plots too, broadly speaking a parallel could be hazarded.

*C. The Amino-acid Nitrogen and Total Nitrogen Ratio of the Wheat Plant during its Ontogenic Drift.*

Fig. 5 gives the ratios of the amino-acid nitrogen/total nitrogen in plants growing in the different soils.

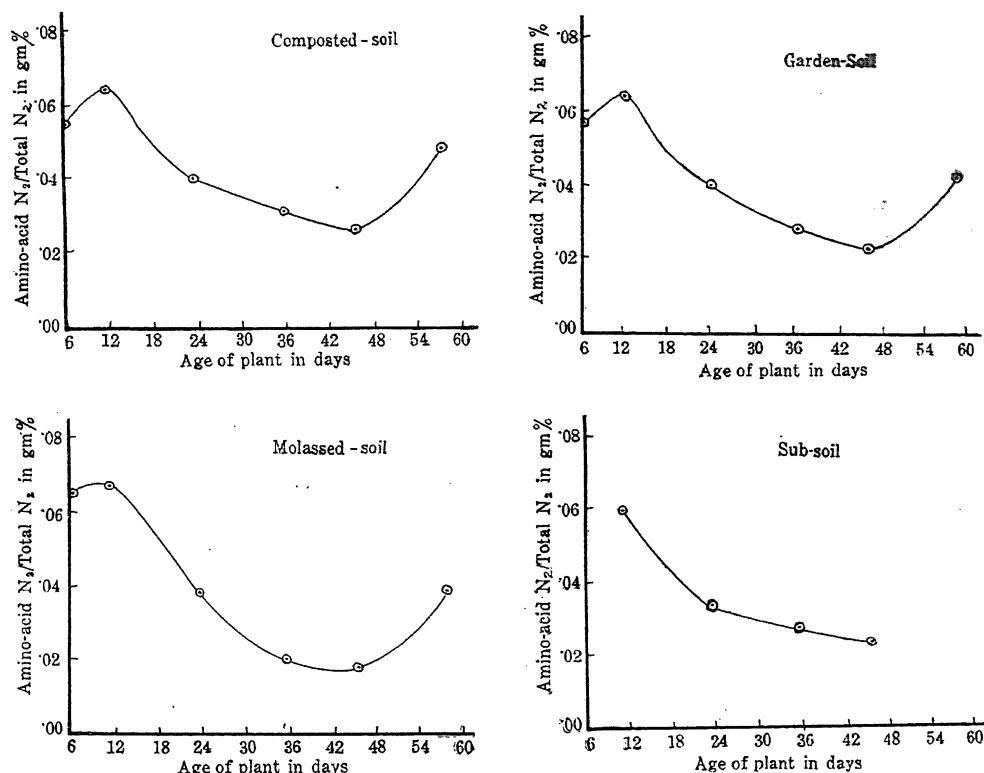


Fig. 5

It is at once apparent that this ratio starts high but gradually descends till the 46th day, showing thereby that the reserve nitrogen increases at the expense of the more mobile amino-acid nitrogen. Just before the fruiting stage, however, there is a sudden rise in the amino-acid nitrogen, which necessarily must be from the breakdown of the higher reserve nitrogen, for the soil nitrogen at this stage has no correlation with the amino-acid nitrogen. The rise is yet more augmented in the young grain and the curves in all the cases rise steeply.

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# PHYSIOLOGICAL STUDIES ON WHEAT PLANT. PART II—THE INFLUENCE OF MOLASSES ON THE NITRIFICATION OF SOIL

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## SUMMARY

1. The unsterilised molassed soils show greater value for total nitrogen over the sterilised ones, with the same amount of molasses, when exposed to sunlight, the maximum amount being 1.33 times

2. The sterilised molassed soils show no change in their total nitrogen for the first 15 days, when exposed to light. Thereafter for 15 days there is a rise and then the total nitrogen again becomes constant till the end of the experiment.

3. The unmolassed unsterilised soil shows a slight rise in total nitrogen both in light and in darkness. This may be due to bacterial or algal activities.

4. The rise in total nitrogen, when molassed soils are exposed to light, may be due to (1) the energy set free in the photo-oxidation of sugars present in the molasses, which causes the fixation of atmospheric nitrogen and (2) bacterial activity.

## INTRODUCTION

Nitrification in soils has been generally accepted to be a bacterial process. Recently, Dhar<sup>2</sup> (1933-36) and his co-workers have shown that nitrification in tropical soil is more photo-chemical than bacterial. The soil is believed to act as catalytic agent. The catalysts in soil can be either organic or inorganic or both. Many mineral substances such as titania, zinc oxide, sodium uranate, alumina and silica have been found to act as photo-catalysts on the oxidation of ammonium compounds. Corbet<sup>1</sup> (1934-35) in England, Allen in Hawaii, Sarkaria and Fazaluddin (1935) in Punjab are in general agreement with Dhar. Fazaluddin<sup>3</sup> reported that the catalytic power varies with different soils and was different for different nitrogenous compounds. According to Fazaluddin soil fats, waxes, resins and humus act as catalysts; sodium and potassium clays are better catalysts than calcium, hydrogen, magnesium and manganese clays. The bacterial nitrification was negligible as compared to photo-nitrification in mono-ethyl-aniline solutions in the presence of soil. Fraps and Sterges<sup>4</sup> (1935) showed only a weak catalytic action with some American soil.

## MATERIAL AND METHOD

### A. *Material*

Ordinary sub-soil, got from a depth of 2 ft. and below, was used in these experiments. Sample of molasses was obtained from the Naini Sugar Factory, Allahabad.

The molasses was very rich in carbohydrate contents and the total nitrogen contents were 0.102 grm. per cent.

### B. Method

In all the sets of experiments, 250 grm. of powdered and sieved soil was taken in 500 c.c. pyrex flasks and 70 c.c. distilled water was added in each. Some of these were treated with different percentages of molasses and some were unmolassed. All the flasks were plugged with cotton wool with a glass rod for stirring the soil. Some of the flasks were sterilised in an autoclave for 45 mts. at 25 lbs. pressure. During the course of investigation it was noticed that complete sterilised condition could only be achieved by autoclaving more than once and for a longer time.

In the first set of experiments, 10 grm. of molasses were mixed with the soil. Some of the flasks were autoclaved and some of the sterilised and some unsterilised molassed soil in the flasks were exposed to sunlight for 6 hours daily. While other sterilised and unsterilised soil in the flasks were kept in dark.

In the second set of experiments, 2 grm. of molasses were mixed and the above-mentioned procedure was followed.

In the third set of experiments, no molasses were added. The sterilised and unsterilised soil in flask were kept both in light and some in dark.

Bacterial examination was made, before each sample was analysed, by Winogradsky's method. The stain used was 1% erythrosin in 5% aqueous phenole solution.

Total nitrogen of the sample was found by the modified Kjeldahl method (Bhattacharya and Ranjan, *Proc. Nat. Acad. Sci.*, X, 65.) To avoid bacterial action, the "wet digestion" method was not followed in these experiments.

### EXPERIMENTAL RESULTS

The results of analysis are given in the following tables.

TABLE I

*250 grm. of soil plus 10 grm. molasses.*

Total nitrogen contents of the soil in grm. per 100 grm. of dry molassed soil.

Dates of analysis	EXPOSED		DARK	
	Sterilised	Unsterilised	Sterilised	Unsterilised
29-9-'38	0.0437	0.0438	0.0438	0.0435
14-10-'38	0.0437	0.0450	0.0437	0.0439
29-10-'38	0.0486	0.0508	0.0435	0.0454
28-11-'38	0.0502	0.0564	0.0437	0.0466
24-12-'38	0.0500	0.0582	0.0437	0.0472

TABLE II

*250 gm. soil plus 2 gm. molasses.*

Total nitrogen contents of the soil in gm. per 100 gm. of dry molassed soil.

Dates of analysis	EXPOSED		DARK	
	Sterilised	Unsterilised	Sterilised	Unsterilised
30- 9-'38	0.0415	0.0416	0.0414	0.0416
15-10-'38	0.0416	0.0422	0.0413	0.0418
30-10-'38	0.0435	0.0452	0.0415	0.0424
30-11-'38	0.0448	0.0484	0.0415	0.0427
25-12-'38	0.0433	0.0495	0.0415	0.0426

TABLE III

*Original soil, unmolassed.*

Total nitrogen contents of the soil in gm. per 100 gm. of dry soil.

Dates of analysis	EXPOSED		DARK	
	Sterilised	Unsterilised	Sterilised	Unsterilised
29- 9-'38	0.0404	0.0405	0.0405	0.0403
15-10-'38	0.0404	0.0407	0.0405	0.0410
31-10-'38	...	0.0431	...	0.0428
30-11-'38	0.0404	0.0412	0.0404	0.0417
24-12-'38	...	0.0406	...	0.0415

## DISCUSSION

*A. Total Nitrogen of Soils exposed to Light.*

The curves of nitrogen increase in soil shows (Fig. 1) that for the first 15 days the value of total nitrogen remains practically constant, thereafter a rapid rise in the nitrogen content is shown. The increase of total nitrogen is greatest in the unsterilised soil containing 10 gms. of molasses. At the end of 86 days the amount of total nitrogen rises to about 1.33 times the original value. In the case of sterilised soil with 10 gms. of molasses, there is again a rise but is proportionally less than the

former case, the increase of nitrogen is about being 1.14 times. Unsterilised soils with 2 gms. of molasses show a similar rise to that soil containing 10 gms. of molasses. For here too, at the end of 86 days the rise of nitrogen is 1.19 times. Similarly, the sterilised soil containing 2 gms. of molasses shows an increase of about 1.04 times. Thus, it is abundantly clear that prolonged exposure to light with molassed soils increases the nitrogen content of soils.

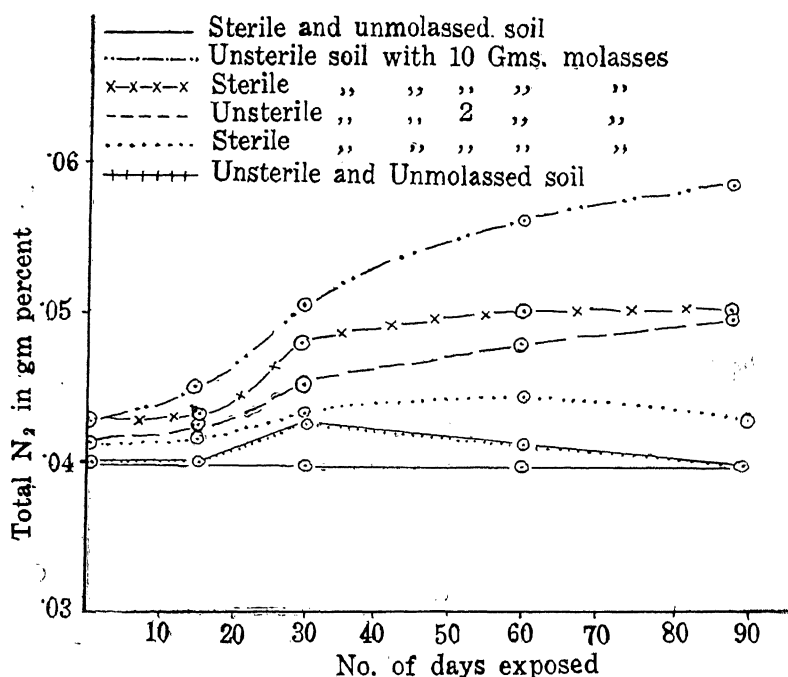


Fig. 1

Fig. 1 also gives the graphs of soils with no molasses. In the case of unsterilised soil with no molasses, the nitrogen content also goes up in light. This evidently is due to bacterial activity, because the sterilised soil do not show any rise in light.

It is thus clear that for increasing nitrogen content of the soil, molasses is necessary. In the absence of molasses, the soil is unable to increase the nitrogen content. The unsterilised soil in which the nitrogen has risen is only a temporary phase, for within 40 days the nitrogen content again fell off to the original value.

#### B. Total Nitrogen of Soils in Darkness.

In the case of the unsterilised soil containing 10 gms. of molasses, like the former case for 15 days, the nitrogen value remains practically constant. Thereafter it increased, and at the end of 86 days it was about 1.10 times the original value. The rise

of total nitrogen in darkness in this case can only be attributed to bacterial activity (see Fig. 2). Similarly, unsterilised soils containing 2 gms. of molasses show a slight

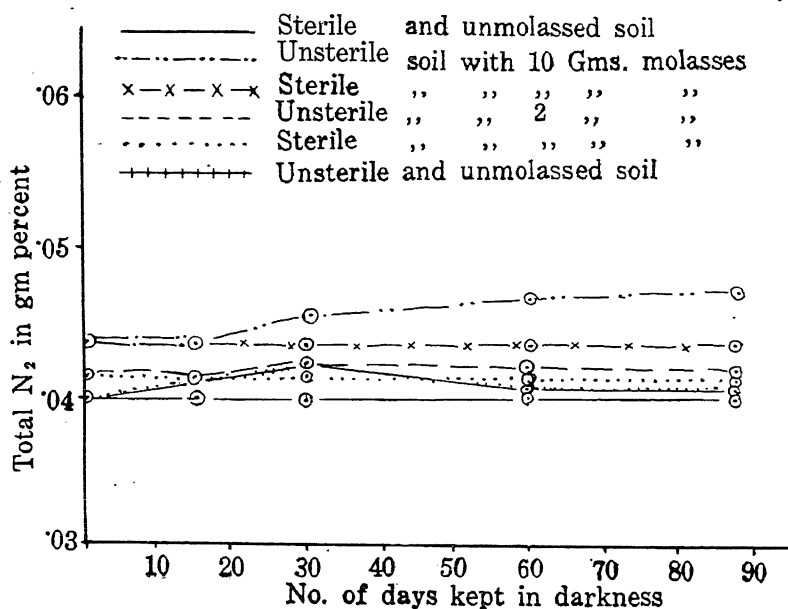


Fig. 2

increase in total nitrogen content. In the case of the sterilised soils containing 10 gms., 2 gms. and no molasses, the results are all similar. No change in the total nitrogen content was noticed throughout the experiment. The unsterilised soil in darkness with no molasses shows a similar increase as in Fig. 1 as with no molasses. It is thus obvious that this temporary increase is not due to the light effect but probably due to the bacterial activity.

### C. The Nitrogen Increase due to Bacteria alone in Light.

The increase of nitrogen in light due to bacterial activity alone in different mixture of molasses is shown in Fig. 3.

The curve is here drawn by taking the difference of the exposed and unexposed unsterilised soils containing similar quantities of molasses and then subtracting from

it the value of total nitrogen increase due to photo-chemical activity. This value then gives the total nitrogen increase due to bacteria in light. From Fig. 3 it is obvious that the bacterial activity goes on increasing to prolonged exposure of light and so also the total nitrogen.

*D. The Increase of Nitrogen due to Photo-chemical Activity.*

The difference of nitrogen values in exposed and unexposed sterilised soils containing similar amounts of molasses gives us the increase of total nitrogen due to photo-chemical activities.

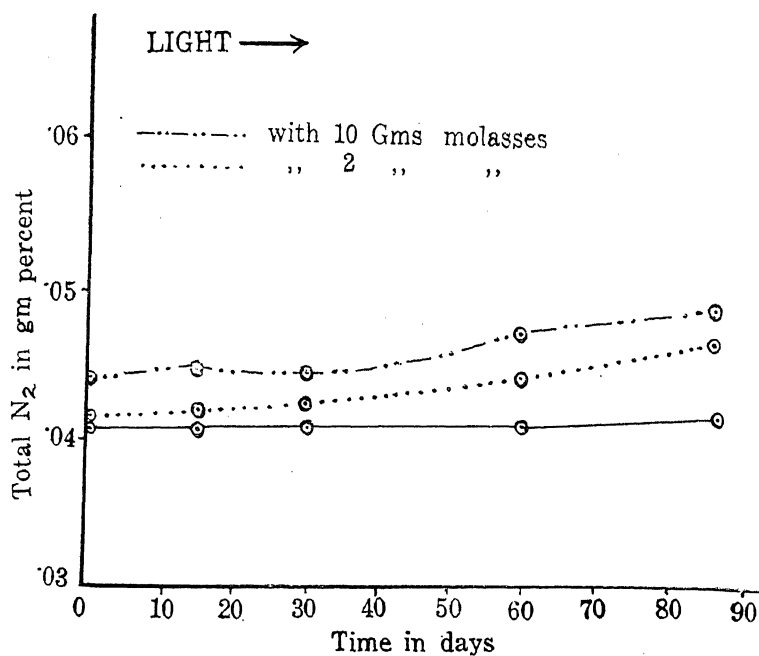


Fig. 3

From Fig. 4 it is apparent that the photo-chemical activity of molassed soil is pretty considerable, for the rise of total nitrogen comes to more than 1.1 times the original value. This rise which is found only in the molassed soil and not in the unmolassed soils may be logically assumed to be due to some photo-chemically oxidisable substance present in a molassed soil. According to Dhar the photo-chemically oxidisable substance may be carbohydrate present in the molasses. The energy given out by the photo-oxidation of these substances is then utilised in combining



the atmospheric nitrogen in the inorganic nitrogenous substances. We can thus finally conclude that the nitrification of molassed soil is brought about by the two

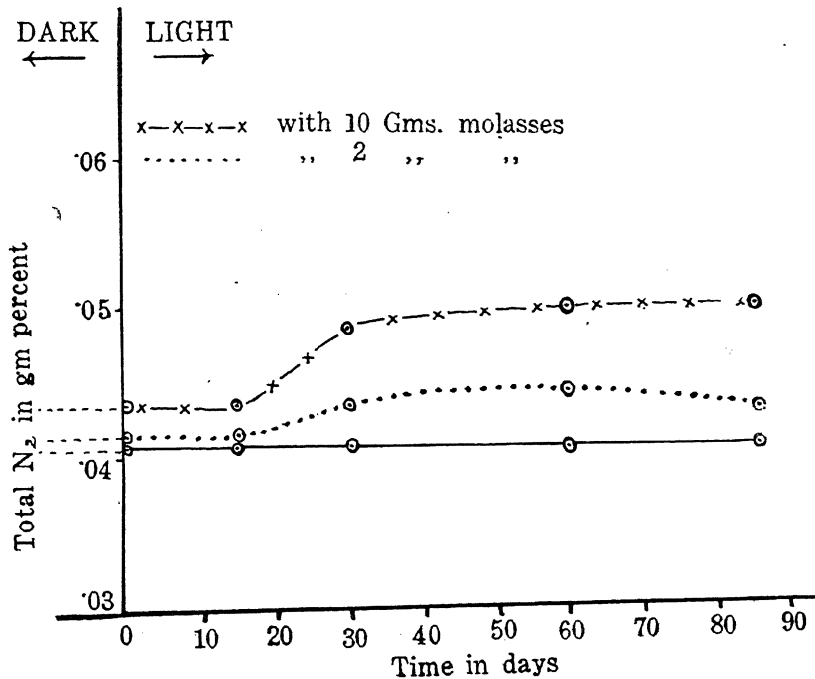


Fig. 4

factors, viz., (1) bacterial activity and (2) photo-chemical oxidation of oxidisable substances like carbohydrates.

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# STRUCTURE AND DEVELOPMENT OF THE MALE AND FEMALE GAMETOPHYTES OF *SESUVIUM PORTULACASTRUM* LINN.

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## SUMMARY

The archesporium in each anther-lobe consists of one to three rows of cells. The primary wall cells form four layers. The hypodermal layer forms the fibrous endothecium and the innermost layer forms the tapetum. The two middle layers degenerate early. The inner wall of the tapetal and endothelial cells undergoes granular cutinisation. Cytokinesis takes place by furrowing. Pollen grains are generally arranged in a tetrahedral manner. Each pollen grain is spherical, psilate and has three germ-pores. The pore membrane from an early stage protrudes out of the germ-pores. The pollen grain is shed at the three-nucleate stage.

The ovule at the mature embryo-sac stage is ana-campylotropous. Up to this stage an air-space in the chalazal region in between the two integuments can be clearly traced. Epidermal cells of the nucellus just below the micropyle stretch out in a radial direction and do not divide periclinally, while the cells surrounding them divide periclinally. The archesporium consists of one to three hypodermal cells. A parietal cell is cut off. The megaspore-mother cell forms generally a row of four megaspores. Sometimes the micropylar dyad does not divide and a row of three cells is formed. The embryo-sac develops from the chalazal megaspore according to the *Normal*-type. The mature embryo-sac is eight-nucleate. The egg is flask-shaped and has the normal structure. The synergids are hooked. The antipodals are three small cells. The two polar nuclei fuse close to the egg-apparatus. Numerous starch grains are deposited in the mature embryo-sac. Hutchinson's view advocating the separation of the Aizoaceae into two families, *Molluginaceae* and *Ficoidaceae*, is supported by embryological evidence.

## INTRODUCTION

The genus *Sesuvium* belongs to the family *Ficoidaceae* of Hutchinson (1926). It comprises about five species distributed along the sea-shores of tropical and subtropical countries. One of the species, *Sesuvium Portulacastrum* Linn., is found abundantly in sandy soils along the Indian coast. The present paper gives an account of the structure and development of the pollen and embryo-sac of this species. It is an extensively creeping herb with opposite, thick and fleshy leaves and pink axillary flowers.

## PREVIOUS WORK

The embryological work on the family Aizoaceae previous to 1934 has been summarized by Bhargava (1934) and two years later by Joshi and Rao (1936). Since then no further work has been done on the family. Following is a brief summary of the main embryological features of the family. For further information reference may be made to Joshi and Rao's (1936) paper.

*Microsporogenesis*.—The anther wall including the epidermis is four layers thick in *Mesembrianthemum pseudotruncatellum* (Schmid, 1925) and five layers thick in *Trianthema monogyna* (Bhargava, 1935). The hypodermal layer in the mature anther forms the fibrous endothecium. The innermost wall layer forms the tapetum. The mature pollen grain as reported by Schmid (1935) in *Mesembrianthemum pseudotruncatellum* is three-nucleate and has three germ-pores.

*Ovule*.—The ovule is ana-campylotropous except in *Trianthema monogyna* (Bhargava, 1935), where it is nearly campylotropous. It has two integuments, but a third integument develops in *Trianthema monogyna* (Bhargava, 1935). Epidermal cap of a distinctive type is formed over the nucellus in the genera *Mesembrianthemum* Schmid, 1925) and *Trianthema* (Bhargava, 1935). The central cells of the epidermis merely elongate, while the lateral cells divide by periclinal walls.

*Megasporogenesis*.—The archesporium mostly consists of a single hypodermal cell. A parietal cell is cut off. Generally a tetrad of four megaspores is formed. A row of three, two megaspores and a dyad, is also observed in some species. In *Trianthema monogyna*, according to Bhargava (1935), the micropylar dyad is generally two-nucleate. The chalazal megaspore always develops into the eight-nucleate embryo-sac. Starch grains are deposited in the mature embryo-sac.

## MATERIAL AND METHODS

The material used in the investigation was obtained from two sources. Some was sent from Bombay by Mr. S. C. Dixit. Another lot was collected from Krusadai Island (S. India) by Dr. A. C. Joshi. In both cases Formalin-acetic-alcohol was used as the fixative. Usual methods were followed to embed it in paraffin. For younger stages sections were cut 7–9 $\mu$  thick and for older stages 10–12 $\mu$  thick. To study the female gametophyte, sections of the gynaecium were cut transversely. Delafield's and Heidenhain's Iron-alum Haematoxylin were used for staining. With the latter stain, picric acid was used for destaining.

## MICROSPOROGENESIS

The primary archesporium, in each of the four anther-lobes, consists of two to three rows of hypodermal cells (Fig. 1). Sometimes a single row of archesporial

cells is also observed. Longitudinally each row consists of approximately five to eight cells. The total number of archesporial cells, therefore, in each lobe of an anther appears to be fifteen to twenty-five. In *Trianthema monogyna*, Bhargava (1935) has recorded only a single row of archesporial cells.

The archesporial cells by periclinal divisions cut off a primary parietal layer just below the epidermis and the primary sporogenous cells on the inner side. The parietal layer now divides by anticlinal and periclinal divisions into two layers. Both of them divide once again periclinally to form four layers (Figs. 2 and 3). These four layers plus the epidermis constitute the wall of the anther (Fig. 4).

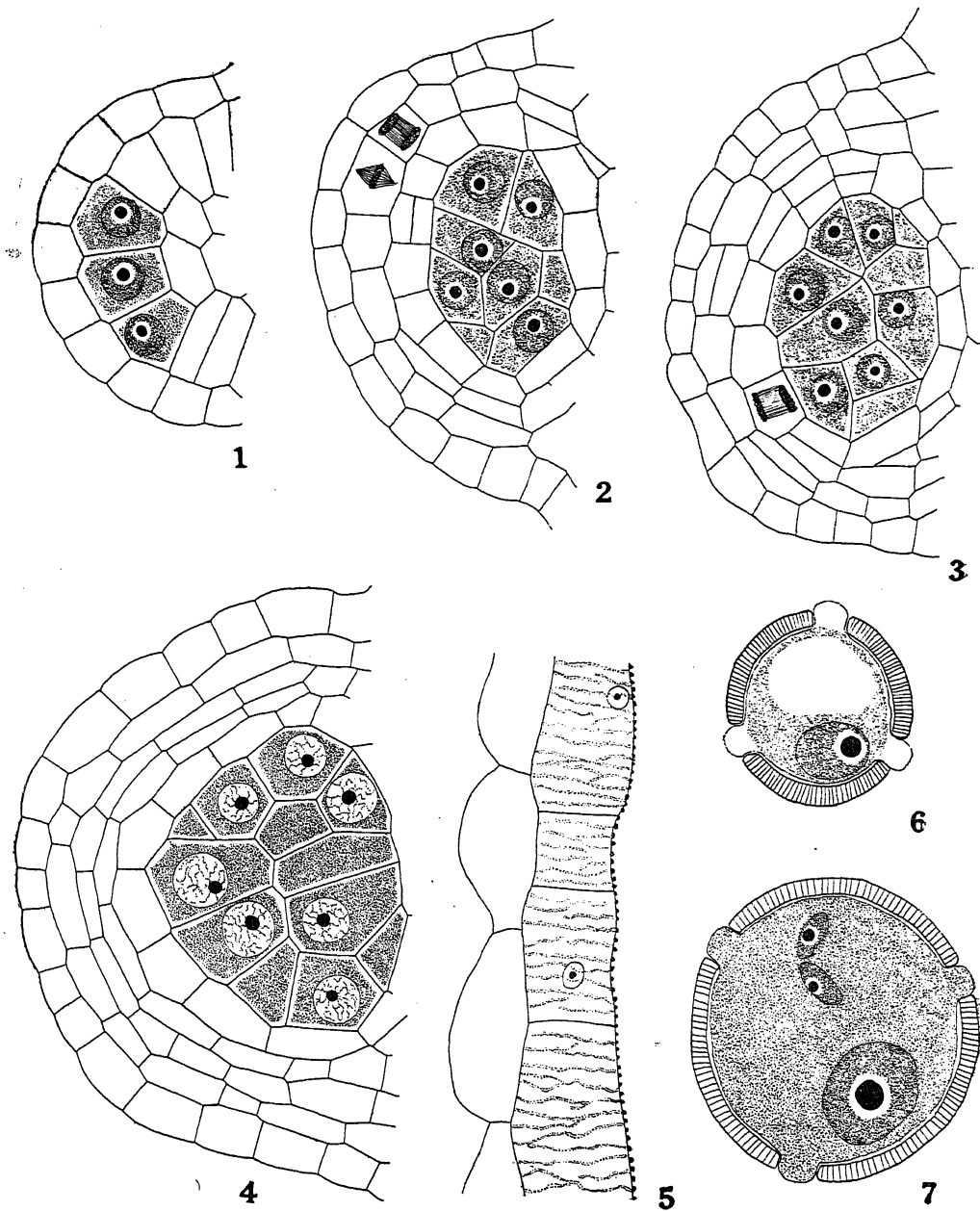
Out of the above four layers, the sub-epidermal layer forms the fibrous endothecium (Fig. 5). As usual the thickening bands in the cells develop as the pollen grains become mature. The two layers inner to the sub-epidermal layer are crushed during the development of the anther. The cells of the innermost wall-layer, which are adjacent to the sporogenous cells, increase in size and in the amount of protoplasm. They begin to take a deeper stain than the rest and develop into the tapetum. During the early prophase of the microspore-mother cells the nucleus of each tapetal cell divides mitotically into two nuclei. The tapetal cells persist in this bi-nucleate condition during the meiotic divisions of the pollen-mother cells. After cytokinesis they become distinctly vacuolate and begin to degenerate. After the two-nucleate stage of the pollen grains no trace of the tapetal cells is seen in the anther. During all this period the cells remain at the periphery and do not leave their place. The tapetum in this species, therefore, is of the secretion type, as in other investigated members of the family.

As previously described the wall of the anther consists of five layers of cells, out of which the outer layer is the epidermis, and the other four are of parietal origin. In majority of the Centrospermales the anther wall is four layers thick, out of which three arise from the primary parietal layer. The difference is due to the fact, that the layer destined to develop into the endothecium in members of the Centrospermales in general, in the present instance divides into two sister layers, and the sub-epidermal layer out of the two, then develops into the endothecium (Fig. 2). As reported by Bhargava (1935), the parietal tissue in the anther of *Trianthema monogyna* also consists of four layers. These two genera, therefore, agree in this respect and differ from the closely related genus *Mesembrianthemum* (Schmid, 1925), where the parietal tissue of the anther consists of three layers only.

During the latter part of anther development characteristic small granular bodies of the nature of cutin appear on the inside of the endothecium and the tapetum. These bodies first appear on the tapetum and then on the endothecium. The author in his work on the embryology of the Amarantaceae (Kajale, unpublished) has discussed the reason for the appearance of these bodies. It appears that they are correlated

PLATE I

L. B. KAJALE—*Sesuvium Portulacastrum* Linn.



Figs. 1—7, *Sesuvium Portulacastrum*. Figs. 1—4, transverse sections of anther-lobes at various stages of development showing the differentiation of the sporogenous and parietal tissues. Fig. 5, a part of a mature anther wall showing epidermis and the fibrous endothecial layer with granules of cutin-like substance on its inner surface. Fig. 6—7, 1- and 3-nucleate pollen grains. Figs. 1—4,  $\times 800$ ; Fig. 5,  $\times 950$ ; Figs. 6—7,  $\times 1600$ .

with the disintegration of the cell walls on the inner side of the endothecium and tapetum. Further support to this idea has been secured from the present investigation. The septum separating the two loculi is another part of anther-lobe, which degenerates during the development of the pollen grains. Correlated with this, similar granular bodies appear on either side of the septum. Such bodies are not recorded in the genera *Mesembrianthemum* (Schmid, 1925) and *Trianthema* (Bhargava, 1935), but it is likely that the authors have missed this point.

While the above changes are taking place in the parietal tissue, a good deal of change take place in the primary sporogenous cells also. They divide once or twice to form microspore-mother cells. The cells do not separate from each other and retain their somewhat polyhedral shape. At this stage between the protoplasm and the cell wall of the pollen-mother cells a new mucilaginous sheath is developed. This is quite thick and with Delafield's haematoxylin stains lighter than the original cell wall.

The two reduction divisions are quite normal. The spindles in the second division are generally at right angles to each other, but sometimes they are also parallel. As soon as the second reduction division is complete, the constriction furrows appear at four places in the periphery of the pollen-mother cells. These gradually progress inwards and the four pollen grains separate off. Depending upon whether the spindles during the second meiotic division are at right angles or parallel to one another, the resulting grains are arranged in a tetrahedral or isobilateral manner.

The pollen grains become spherical in shape from a very early stage, i.e., soon after they are separated off from each other. Each pollen grain develops its usual intine and exine. The latter is quite smooth and does not bear any spines or ridges (Figs. 6 and 7). The pollen grains, therefore, may be described as psilate in character. Each pollen grain generally has three germ-spores placed at an equal interval (Figs. 6 and 7), as in *Mesembrianthemum* (Schmid, 1925), *Mollugo* (Bhargava, 1934) and *Trianthema* (Bhargava, 1935). The pollen grains in this family thus differ in the number of germ-spores from the members of the Chenopodiaceae and Amarantaceae.

The intine slightly protrudes out of the germ-pores even from the uni-nucleate stage (Fig. 6). In the early stages the pollen grain is vacuolate at one end. The nucleus divides at the periphery and one of the nuclei is cut off for some time by a wall, thus forming a generative cell. After the wall separating the generative cell, has disappeared, the pollen grain is once more filled with cytoplasm. The generative nucleus divides and two male nuclei are formed (Fig. 7). Presence of nucleolus is also observed in the naked male gametes. The latter are spindle-shaped in form. The pollen grains are shed at this stage. Each pollen grain measures 25-30 $\mu$  in diameter.

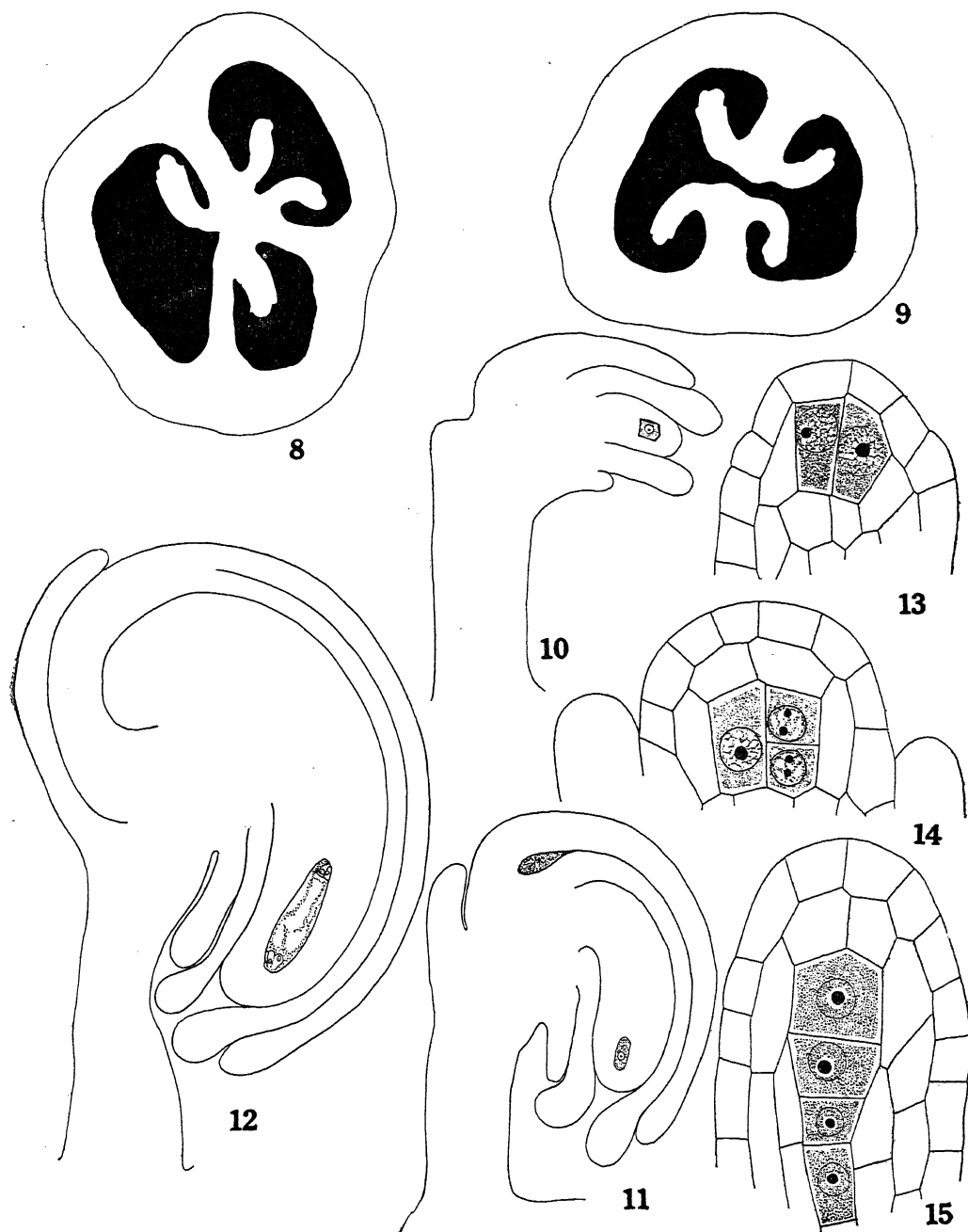
## THE OVULE

The ovary is either bi-carpellary or tri-carpellary and is imperfectly bi-locular or tri-locular (Figs. 8 and 9). In one case it was found to have four loculi. Numerous ovules are present in each loculus and they are borne on axile placentae. Generally two or three septa begin to develop from the wall of the ovary. Before they meet, the ovules begin to develop from them as lateral outgrowths (Fig. 9). The septa fuse in the basal part of the gynaecium (Fig. 8). In the upper part of the ovary, however, these septa do not develop so much and remain apart. The ovary, therefore, in the upper part remains uni-locular. It was clearly observed to be so up to the fertilization stage. Probably it continues to remain so even in the mature fruit. The epidermal cells at the tips of these septa, which come nearly to the centre, are slightly different from the rest. They are elongated and larger than others and form part of the transmitting tissue of the gynaecium.

Each ovule develops as a small protuberance and shortly afterwards the integuments begin to appear. This happens at the time when the archesporium differentiates (Fig. 13). When both the integuments have covered almost the greater part of the nucellus, a third integument or aril begins to develop from the base of the outer integument (Fig. 10). Bhargava (1935) also reports the presence of such an aril in *Trianthema monogyna*, while in *Mollugo nudicaulis* (Bhargava, 1934) the third integument is absent. The aril is mostly four to five layers thick and at about the mature embryo-sac stage covers nearly  $1/3$  of the ovule (Fig. 12). Of the two integuments, the inner one only forms the micropyle, as in the Centrospermales in general (Figs. 11 & 12). This integument is mostly two layers thick, but in the micropylar part it is slightly thicker. The outer integument like the inner one is also two cells thick through its greater length, but in the region of the micropyle and in the chalazal region it is thicker. In the latter portion its thickness varies from three to four layers of cells. As the embryo-sac becomes mature, some small grains of the nature of tannin begin to be deposited in two layers of the integuments, namely, the outer layer of the outer integument and the inner layer of the inner integument and then in the inner layer of the inner integument. In the outer layer their deposition begins from the chalazal end and progresses towards the micropyle. In the inner layer the grain deposition begins later. It starts from the micropylar end and extends towards the chalaza. In the early stages of ovule developments a prominent air-space is seen in the chalazal region in between the two integuments (Fig. 11). The presence of this space can be clearly seen up to the mature embryo-sac stage, and at this stage it slightly increases in size also. In *Mollugo nudicaulis* (Bhargava, 1934) the presence of a similar air-space can be made out from the figures of Bhargava (1934, text Fig. 1), though the author has not made any mention of this point in the text. The same author (Bhargava, 1935)

PLATE II

L. B. KAJALE.—*Sesuvium Portulacastrum* Linn.



Figs. 8—15, *Sesuvium Portulacastrum*. Figs. 8—9, transverse sections of 2- and 3-locular gynaecia showing young ovules arising from the margins of the septa. Figs. 10—12, different stages in the development of the ovule. Figs. 13—15, primary archesporial and megaspore-mother cell stages. In fig. 15 the megaspore-mother cell is at the end of a row of four supporting cells. Figs. 8—9,  $\times 750$ ; Figs. 10,  $\times 210$ ; Figs. 11—12,  $\times 150$ ; Figs. 13—15,  $\times 950$ .



does not say any thing about the air-space in *Trianthema monogyna*, nor do his figures give any indication of its presence.

The nucellus is quite massive. At the seven-nucleate stage of the embryo-sac it consists of two layers of cells above the embryo-sac, four to six layers of cells at the sides and twenty to thirty layers of cells towards the chalazal end. The behaviour of the nucellar epidermis is quite different from many plants of the Centrospermales. In a large number of plants, e.g., *Amarantaceae* (Kajale, unpublished), *Chenopodiaceae* (Kajale, unpublished), *Nyctaginaceae* (Kajale, 1938), *Gisekia pharnaceoides* (Joshi and Rao, 1936), the epidermis divides to form a cap over the nucellus. In the present instance, the epidermal cells just below the micropyle do not divide periclinally, but become much elongated radially (Fig. 25). The other epidermal cells surrounding them, however, divide in a periclinal fashion. This corresponds to what is observed in *Trianthema* (Bhargava, 1935) and *Mesembrianthemum* (Huber, 1924; Schmid, 1925). Joshi and Rao (1936) think that this character is distinctive of the Ficoidaceae of Hutchinson (1926). The present investigation supports this contention. The form of the ovule at the mature embryo-sac stage is shown by Fig. 12. The figures 10 and 11 show two stages in its development. At the mature embryo-sac stage the ovule has an ana-campylotropous form (Fig. 12) and is provided with a long funicle.

#### MEGASPOROGENESIS

The archesporium in the young ovule differentiates at an early stage. Some of the hypodermal cells increase in size, begin to take a deeper stain and develop into the archesporium. Their number is generally two or three (Fig. 13), but in a few cases only one archesporial cell was observed. In *Trianthema* (Bhargava, 1935) and *Mollugo* (Bhargava, 1934), there is only one archesporial cell. All the archesporial cells do not cut off a parietal cell except occasionally. Only one does so, and form a megaspore-mother cell and a parietal cell (Fig. 15). In one case, two megaspore-mother cells were observed in a single nucellus (Fig. 14). Still in another these two megaspore-mother cells had developed simultaneously up to the dyad stage (Fig. 20). The fact that cases like these are observed here and there, strongly supports the multicellular nature of the archesporium in the plant under investigation.

The megaspore-mother cell gradually increases in size and in the early stages rests on a row of supporting cells (Fig. 15). After it has reached its maximum size (Fig. 16), it divides by a transverse wall to form two dyad cells (Fig. 17). Both these dyad cells divide once again and a regular linear row of four megaspores is formed (Fig. 18). Sometimes, however, the upper dyad cell may not divide, and a row of one dyad and two megaspores only is formed (Fig. 19).

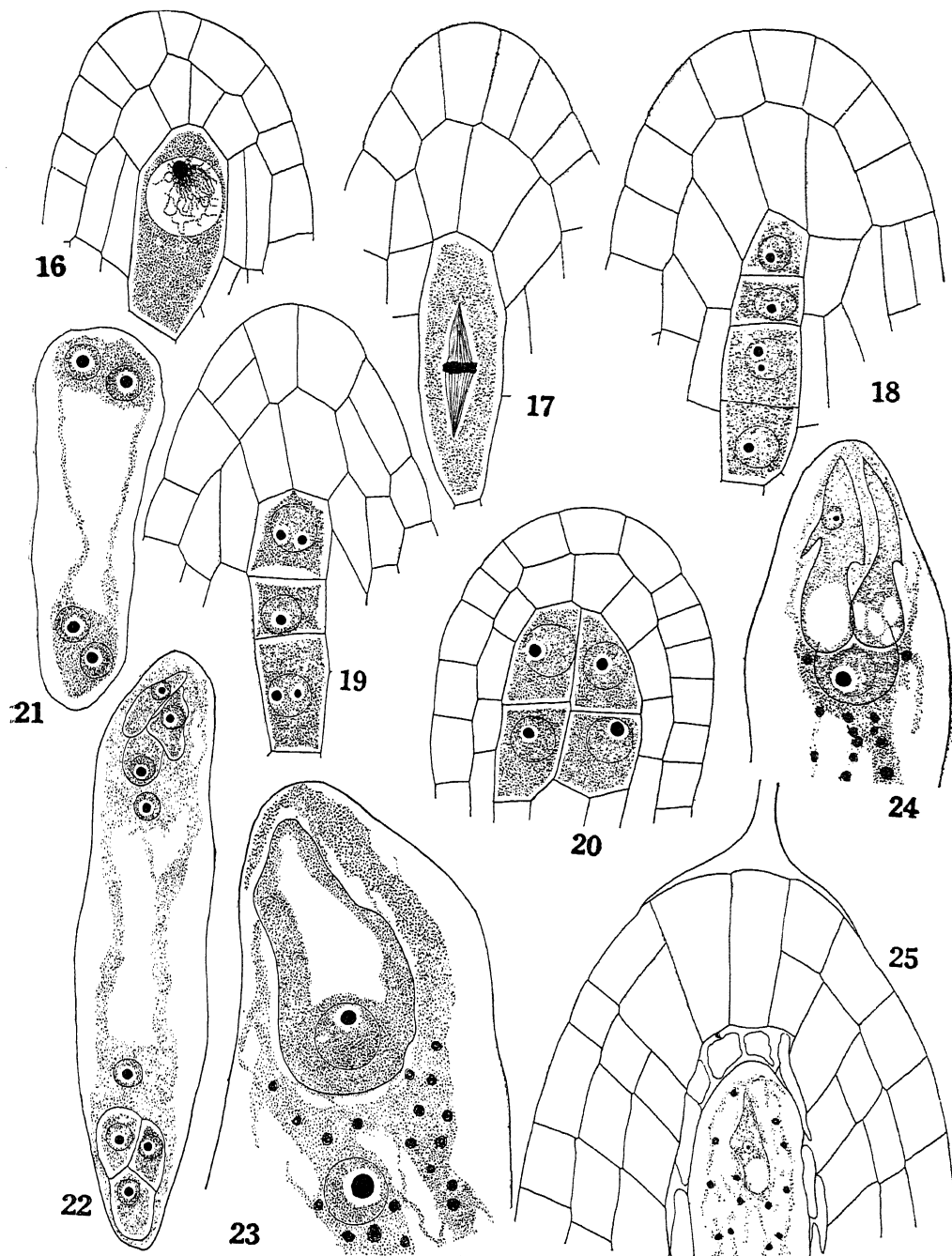
The megaspore at the chalazal end always develops in the embryo-sac, while the three micropylar megaspores degenerate. The functioning megaspore passes as usual through the two- and four-nucleate stages (Fig. 21). When the latter condition is reached, all the nuclei of the embryo-sac divide once again and give rise to a typical eight-nucleate embryo-sac (Fig. 22).

The egg is a broad flask-shaped structure. It has a prominent vacuole in the micropylar end. The nucleus with most of the cytoplasm is present in the chalazal region (Fig. 23). The two synergids possess rather acute hooks (Fig. 24). The portion above the hooks is somewhat elongated and contains the nucleus and cytoplasm. The chalazal part of the synergids is occupied by a large vacuole. The two polar nuclei fuse below the egg-apparatus (Fig. 23). It is, therefore, evident that the chalazal polar nucleus moves quickly over to the micropylar end. The antipodals are three small cells placed at the extreme chalazal end. The presence of starch grains in the mature embryo-sac has been seen in Aizoaceae in *Trianthema monogyna* (Bhargava, 1935), *Tetragonia expansa*, *Mesembrianthemum linguiformis* (Huber, 1924), *M. pseudotruncatellum* (Schmid, 1925), and *Aizoon canariensis* (Dahlgren, 1927). Similar starch grains have also been observed in the present plant (Figs. 23—25).

#### DISCUSSION

Whether the plants allied to the genus *Mollugo* on the one hand and those allied to the genera *Aizoon*, *Trianthema*, *Mesembrianthemum* and *Sesuvium* on the other, should all be placed in one family, is now a point for discussion among taxonomists. Engler and Prantl (1889) and many others place all these plants in one family Aizoaceae, while Hutchinson (1926) separates these into two families, Molluginaceae and Ficoidaceae. Joshi and Rao (1936) from the review of the embryological characters of these plants found that the members of the Molluginaceae of Hutchinson (1926) differ in two embryological features constantly from those of the Ficoidaceae. In *Mesembrianthemum*, *Trianthema*, and *Tetragonia*, the cells of the nucellar epidermis just below the embryo-sac do not divide, but simply stretch out radially, while the cells surrounding them undergo periclinal divisions. Secondly the mature embryo-sac is full of starch grains. In *Mollugo*, on the other hand, all the cells of the epidermis of the nucellus divide periclinally and the central cells are of the same size as the surrounding ones, and there is no deposition of starch grains in the embryo-sac. From this they concluded that the embryological evidence supports the view of Hutchinson (1926).

The present study of the gametophytes of *Sesuvium Portulacastrum* shows that this genus, which has been placed in Ficoidaceae by Hutchinson (1926), closely agrees with the genera *Trianthema*, *Mesembrianthemum* and *Tetragonia*. The structure of the nucellar epidermis is the same, and there is a similar deposition of starch



Figs. 16—25, *Sesuvium Portulacastrum*. Fig. 16, megaspore-mother cell. Fig. 17, the same undergoing the I meiotic division. Fig. 18, a linear tetrad. Fig. 19, a linear row of a dyad and two megaspores. Fig. 20, two dyads in the same nucellus. Fig. 21—22, four- and eight-nucleate embryo-sacs. Fig. 23, apex of a mature embryo-sac showing the egg, secondary nucleus and starch grains. Fig. 24, the same showing the complete egg-apparatus and starch grains. Fig. 25, apex of the nucellus showing the formation of the characteristic epidermal cap.  $\times 950$ .

grains in the mature embryo-sac. Further, it exactly resembles *Trianthema* in the development of an aril around the ovule. Thus this study further supports the conclusions of Joshi and Rao (1936).

In conclusion, the writer desires to express his indebtedness to Dr. A. C. Joshi for the material and guidance during the investigation. He is also thankful to Mr. S. C. Dixit, of Wilson College, Bombay, for part of the material.

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## SUMMARY

THE ORIGIN AND FUNCTION OF THE "SECONDARY NUCLEI." *By D. R. Bhattacharya and  
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1. The secondary nuclei in the eggs of the Hymenoptera examined arise in very early oocytes in close proximity to the nucleus.
2. The plasmosomes of the early oocytes undergo repeated divisions and throw out the buds into the cytoplasm. These buds give rise to bodies, simulating true nuclei.
3. The secondary nuclei move to the periphery in advanced eggs.
4. The secondary nuclei themselves emit nucleolar particles, which in one case (*Scolia*) give rise to a fresh generation of secondary nuclei.
5. Bodies resembling secondary nuclei are found at the base of the follicular cells in *Polistes*.
6. At the periphery of advanced eggs certain vacuolar bodies are found to arise independently, which later on form secondary nuclei.
7. The secondary nuclei do not give the chromatin test with Feulgen's method.
8. They ultimately disappear without transforming into yolk.

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*N.B.*—The above summary of the paper which was read at the annual meeting of the Academy 1940, was inadvertently left out from the Business Matter 1939.